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**TECHNICAL REPORT
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THE USE OF OXYGEN SCAVENGERS AND ACTIVE PACKAGING TO REDUCE OXYGEN WITHIN INTERNAL PACKAGE ENVIRONMENTS

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CONTENTS

	<u>Page</u>
FIGURES	vii
TABLES	ix
PREFACE	xi
ABBREVIATIONS, ACRONYMS AND SYMBOLS	xiii
 SUMMARY	 1
 INTRODUCTION	 2
1. Developmental Approach	3
2. Rationale for In-Package Oxygen Scavenging	5
A. Food Deterioration	6
i. Microbiological Deterioration	6
ii. Enzymatic Deterioration	6
iii. Biochemical Deterioration	6
3. Measures to Exclude Oxygen	7
4. Oxygen Entry After Closure	9
5. Historical Background	9
A. Early Work	10
B. 1970s	11
C. 1980s	11
D. 1990s	13
6. Commercial Applications	14
7. U.S. Military Applications	16
8. Japanese Situation	16
 CRITICAL ANALYSIS OF OXYGEN SCAVENGER SYSTEMS	 22
1. Definitions	22
A. Antioxidants	22
B. Interceptors	23
C. Absorbers	23
D. Scavengers	23
2. Antioxidants	24
3. Sulfites	25
4. Boron	29
5. Glycols and Sugar Alcohols	29

iii

Accession For	
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CONTENTS (CONTINUED)

	<u>Page</u>
6. Unsaturated Fatty Acids and Hydrocarbons	30
7. Palladium Catalysts	33
8. Enzymes	33
9. Yeast	42
10. The Package Material as a Reducing Agent	42
11. Ferrous Iron-Based Absorbers	44
A. American Organizations	46
i. Multiform Desiccants	46
ii. United Desiccants	48
iii. Engelhard	48
iv. Amoco Chemical	48
v. Liquid Air	49
B. Japanese Organizations	49
i. Mitsubishi Gas Chemical	49
ii. Toyo Seikan	53
iii. Sumitomo Chemical	57
iv. Toppan Printing	57
C. European Organizations	58
i. PLM	58
ii. Atco SA	58
12. Economics	58
13. Developmental	59
A. Ascorbic Acid-Based Absorbers	60
i. Pillsbury	61
ii. W.R. Grace & Company	61
B. Japanese Organizations/Companies	62
C. Oxbar™	63
D. Aquanautics/Advanced Oxygen Technologies (AOT)	67
E. Photosensitive Dyes	76
F. End Product Scavengers	81
CONCLUSIONS	83
1. Commercial Applications	84
2. Oxygen Removal Chemistries	84
RECOMMENDATIONS	87

CONTENTS (CONTINUED)

	<u>Page</u>
APPENDICES	
Appendix A	Survey Form: End Users of Oxygen and Moisture Scavengers 93
Appendix B	Survey Form: Suppliers of Oxygen and Moisture Scavengers 99
Appendix C	Relevant Patents 107
BIBLIOGRAPHY	110
DISTRIBUTION LIST	120

FIGURES

		<u>Page</u>
Figure 1	Ligand/Metal Complex Shown Binding Oxygen	68
Figure 2	Schematic Representation of Immobilization and Activation of AOT's Scavenger on a Silica-Based Insoluble Support Structure (Activation by Divalent Metal Ion)	69

TABLES

		<u>Page</u>
Table 1	Classification of Oxygen Absorbers in Japan	18
Table 2	Oxbar: Oxygen Scavenging System	64

PREFACE

The following final technical report details the market investigation performed by Rubbright-Brody, Inc. under Contract Number DAAK60-94-P-0891. During the period 14 March to 20 September 1994, two primary investigators worked on the project to determine the commercial availability of technologies of incorporating oxygen scavengers into packaging materials in order to retain quality of food contents.

Natick Project Office responsible for monitoring this contract was Ms. Lauri Pruskin of the Packaging Systems Branch (PSB), Sustainability Directorate (SusD).

Citation of trade names in this report does not constitute an official endorsement or approval of the use of such items.

ABBREVIATIONS, ACRONYMS AND SYMBOLS

atm	Atmosphere
a_w	Water activity
°C	Degrees Celsius
Ca	Calcium
CaCl_2	Calcium chloride
Ca(OH)_2	Calcium hydroxide
cc	Cubic centimeters
cm^2	Square centimeters
Co	Cobalt
CO_2	Carbon dioxide
dm^2	Square decimeter
e.g.	For example
EVA	Ethylene vinyl acetate
EVOH	Ethylene vinyl alcohol copolymer
°F	Degrees Fahrenheit
Fe	Iron
Fe_2O_3	Iron oxide/ferrous oxide
FeSO_3	Iron sulfite/ferrous sulfite
FDA	Food and Drug Administration
ft.^2	Square feet
i.e.	That is
in.^2	Square inches
g	Grams
G	Enzyme substrate, glucose
GRAS	Generally recognized as safe (by FDA)
H or H_2	Hydrogen
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
Hg	Mercury
Kg	Kilogram
μl	Microliter
$\mu\text{l/day}$	Microliters/day
μm	Micrometer
μmoles	Micromoles
m^2	Square meter
mg	Milligrams
ml	Milliliter

ABBREVIATIONS, ACRONYMS AND SYMBOLS (CONTINUED)

mm	Millimeter
min.	Minute
MnCl ₂	Manganese chloride
MXD6	Symbology for high oxygen barrier resin
NaCl	Sodium chloride/salt
O ₂	Oxygen
OPET	Oriented polyester (film)
OPP	Oriented polypropylene (film)
P	Permeation coefficient
PET	Polyester
PP	Polypropylene
ppb	Parts per billion
ppm	Parts per million
PS	Polystyrene
psig	Pounds per square inch (gauge)
PVDC	Polyvinylidene chloride/saran
SO ₂	Sulfur dioxide
SO ₃	Sulfur trioxide/sulfite

SUMMARY

Technologies and commercial applications of oxygen scavenging for packaged foods were reviewed comprehensively to determine the potential to incorporate them into package materials and structures. The ability to continuously remove oxygen from package interiors could significantly enhance contained food product quality or prolong shelf life. To date, the most important commercializations have been the inclusion of iron or ascorbic acid powders in gas permeable sachets or packets for insertion within barrier packages of food. Most of these developments and commercial applications have been offshore, largely in Japan where oxygen scavenger sachets in food packages are not uncommon to better retain product content quality.

Commercial incorporation of oxygen scavengers into package materials and structures has been confined commercially to blending into glass bottle closure liners. Developments have been underway to introduce oxygen scavengers into other package material structures such as films and plastic bottle, jar and tray body walls. Although most of this activity has been offshore in Japan and Europe, since 1993 American companies have been working in this area. Amoco Chemical Company, Multiform Desiccants, Inc. and W. R. Grace & Co. all have active development programs aimed at combining oxygen scavengers into package materials or structures. Multiform Desiccants and Amoco Chemical hope to have commercial materials available in 1995. Development has been resumed on the previously abandoned Carnaud MetalBox Oxbar™ nylon MXD6/ cobalt/ oxygen removal system.

Favorable quality retention results from inclusion of oxygen scavenger sachets in food packages suggest that extension of the concept into package materials could be beneficial for contained foods. Although few definitive results have been reported from the technology, those limited reports from the Oxbar™ work indicate effective long-term reductions to zero oxygen within the package.

Oxygen scavenging by active package materials and structures has the potential to achieve the objective of enhanced and prolonged quality retention. Considerable development must be performed to confirm this conclusion and to ensure better safety and long-term efficacy. Comprehensive programs by the current United States' developers should be the most efficient route to deliver commercial package structures for military ration packaging applications.

INTRODUCTION

Protection of packaged food contents for extended periods under any prolonged chilled or ambient temperature conditions requires a series of interrelated actions:

1. The product itself must be processed in a manner to stabilize it against enzymatic, microbiological and biochemical activity, with the former two of concern primarily in foods for short-term chilled distribution.
2. The product must be protected against recontamination by active biological vectors of deterioration such as viable enzymes or microorganisms, usually by hermetic sealing.
3. The package generally should be a high gas barrier structure which is hermetically closed, i.e., the seal is not a route for gas transmission into the package or recontamination.
4. The environment within the hermetically sealed package should be free of oxygen, which is not always an easy task since most foods themselves contain occluded and dissolved air, and finite reactable quantities of oxygen are usually present in the package headspace or product interstices if a headspace is not present.

Recognizing that residual oxygen can react biochemically with contained food and cause long-term adverse oxidative effects, which increase as the temperature rises, barrier and vacuum packaging have been supplemented in recent years by active packaging.

Although the term "active packaging" has been used for only about the past 10 years, the concept has been tested or employed for more than 30 years. Active packages are defined as package structures which sense the environment and directly or indirectly respond to it by some physical or chemical action intended to further protect the contained product. The most common active packaging is the incorporation of desiccant pouches within sealed packages of products sensitive to moisture. The desiccant chemicals absorb residual water vapor and any further moisture that may enter the package by permeation or other forms of gas/vapor transmission. Desiccants to protect against excess water vapor have been commercial and widely used for many decades, and so are not discussed in detail in this report which focuses on oxygen removal.

Other forms of active packaging have included: in-packet sachets for carbon dioxide absorption and carbon dioxide generation, both of which are sometimes

employed in modified atmosphere packaging of chilled respiring foods; and ethylene absorption, which is often used in removal of this active respiratory gas from the environment of fresh fruit for long shipment. Other active packaging forms have been used and proposed, such as bags of ethylene absorbers in pallet loads of fruit and the incorporation of oxygen absorbers in bottle closures.

Beyond moisture removal, the most important active packaging objective has been removal of oxygen using techniques variously called absorption, interception or scavenging. Because very long-term stability of ambient temperature-distributed foods is highly dependent on reducing or eliminating oxygen reactions, the U.S. Army Soldier Systems Command (SSCOM), Natick Research, Development & Engineering Center (NRDEC) has had interest in such technologies for military rations.

Although several technologies for actively removing oxygen or scavenging oxygen from package interiors have been discussed for more than 60 years, actual reported physical testing dates back only to the 1950s and real commercialization only to the late 1970s. When Japan's Mitsubishi Gas Chemical Company incorporated their "Ageless" reduced iron gas permeable sachets into larger packages of foods in 1977, active packaging oxygen scavenging became prominent as a commercial technology to help preserve contained foods.

As a result of the many presentations, reports, patents, and claims of the late 1980s and early 1990s on the efficacy of oxygen scavengers, the NRDEC instituted programs to determine their applicability to military ration packaging. Some baked goods rations are now packaged with internal sachets containing reduced iron particles. The relative merit of this approach led to the desire to carry the concept forward beyond loose sachets within packages. Further, insertion of a sachet requires an extra step plus inspection to ensure the sachet is present. If an active oxygen scavenger could be included into a sachet, then it might be possible to incorporate it into a package material. Questions were raised, not only by the military but also by commercial interests and regulatory officials, on the safety of loose sachets, i.e., would the sachet contents be mistaken for a food seasoning or component - although the contents are generally not toxic even if inadvertently consumed (except by an infant).

As a consequence of the desire to employ structures which marry scavenging technology to actual package materials, NRDEC commissioned this study intended to identify the available technologies and to judgmentally evaluate them on the basis of the probabilities of incorporating them directly into package structures. This report is the result of that charter.

1. Developmental Approach

This study represents a comprehensive review of all available secondary sources,

dating back to the origins of oxygen scavenging to the present, by a team of professionals with many years of education, training and direct experience in packaging, active packaging and oxygen scavenger packaging.

The objective has been to provide a situation analysis and assessment of the potential for the commercial availability of oxygen scavengers in package materials. Our results are based on: our experience; prior private client studies in which components that are not proprietary are employed; a review of the relevant secondary information sources; a mail survey to both suppliers and packagers in the United States; and personal interviews with both suppliers and packagers. Our focus was on domestic United States' sources, but the available products in this category are so relatively limited that, with agreement by NRDEC, we have included considerable inputs on offshore developments plus our assessments of their potential for the United States' market. Also included is a list of sources and references which may be used for in-depth probing in the future.

Included in the literature survey is a thorough review of world patents, many of which were not reported in other forms of publication or were not further pursued by the inventors for one or another commercial reasons.

Written surveys were conducted among all companies identified as being active in commercial oxygen scavenging packaging in the United States. Telephone and face-to-face interviews were conducted by us with all known knowledgeable professionals experienced in oxygen scavenging packaging.

The study began with a search of several computer data bases to try to capture the secondary sources, followed by a computer search of the patent literature. Complete copies of more than 100 patents were reviewed. Copies of what we regarded as the most significant patents are included in Appendix C of this report. Copies of the relevant articles which we did not already have were obtained and reviewed. It is interesting to note that many of the literature citations were repeats derived from single commercial press releases or presentations.

The perspective employed by us in this project is the objective of packaging foods in materials that contain oxygen scavenger additives that can remove internal headspace oxygen or could intercept oxygen entering the package by permeation or through flaws in the package structure.

Recognizing that the basis for the ultimate application of oxygen scavengers in materials resides in the principles derived from sachets, a discussion of sachets is included as background. Sachets may be regarded as antecedents to internal labels which, in turn, precede package material structures incorporating oxygen scavengers.

Also included is some discussion on the use of oxygen scavengers in closure liners and compounds which again are both possible antecedents of incorporating the scavengers into the package material structure.

Additionally, a brief on scavenging of aldehydes, i.e., oxidation end products, is included.

2. Rationale for In-Package Oxygen Scavenging

As much as oxygen is necessary for life, it is also an element that is a major factor in food product degradation. Oxygen is involved in anabolic reactions such as respiration and is also very much a part of catabolic or deteriorative reactions of foods.

The reactions of oxygen in catabolysis are integral to the deterioration of foods and beverages. Since most food and beverage products are biological in origin, it follows that their beginnings were in some way oxygen involved, and that they ultimately revert back to their components through oxidative reactions.

Much of the effort dedicated to the preservation of foods and beverages is targeted toward elimination or exclusion of oxygen which would otherwise exert adverse effects. Among the many adverse end effects of oxygen on and in foods and beverages are:

1. Oxidative rancidity of unsaturated fats leading to off-flavors and even, in extreme circumstances, to toxic end products
2. Loss of ascorbic acid or vitamin C, especially in fruit- and vegetable-based foods
3. Darkening and browning of fresh meat pigments
4. Fostering growth of aerobic spoilage microorganisms
5. Staling odors in soft bakery goods
6. Hatching of insect eggs and growth of insects
7. Acceleration of fresh fruit and vegetable respiration
8. Enzymatic and non-enzymatic browning of fresh fruit flesh
9. Oxidation of aromatic flavor oils of beverages such as coffee and tea

In effect, most foods and beverages are in one or another way adversely affected by the presence of oxygen which reduces nutritional content or degrades color, flavor or texture or combinations of these.

A. Food Deterioration

Among the vectors of food deterioration are **microbiological**, often by the presence of oxygen to provide the environment for the growth of aerobic or "oxygen-loving" microorganisms; **enzymatic**, in which biologically catalyzed oxidative reactions require the presence of oxygen; and **biochemical** in which uncatalyzed oxidation reactions usually require the presence of oxygen. Thus, oxygen plays a role in many, if not most, spoilages and quality losses of foods.

i. Microbiological Deterioration

Microbiological deteriorations are usually spoilages that take place in foods with high water activity at temperatures above the foods' freezing point. As the temperature increases, the rate of microbiological growth and hence spoilage, increases geometrically usually up to the temperature at which the microorganisms is thermally disrupted. Most spoilage microorganisms are aerobic and so consume oxygen in their respiratory actions. Thus, the reduction or removal of oxygen from the environment of aerobic microorganism reduces their rate of growth and thus the rate of spoilage. This reduced rate of microbiological growth under reduced oxygen conditions is among the reasons for the effectiveness of vacuum and modified atmosphere packaging for non-sterile foods. On the other hand, complete removal of oxygen can result in conditions under which anaerobic spore forming microorganisms and particularly pathogenic types are capable of growing and producing toxins. Thus, oxygen reduction to retard microbiological spoilage could lead to an undesirable result in food products whose water activity is sufficiently high to permit microbial growth.

ii. Enzymatic Deterioration

Foods whose enzyme systems have not been inactivated by heat or analogous input are vulnerable to deterioration accelerated by biological catalysts or enzymes. In normal respiration, again in foods with sufficiently high water activity, many enzymatic reactions are oxidations and so require the presence of oxygen to take place. Among the types of reactions in which enzymes are involved are browning/discoloration, vitamin C deterioration and flavor loss. Removal of oxygen thus can assist in reducing enzymatic oxidative food deterioration.

iii. Biochemical Deterioration

Even when all biological vectors such as microorganisms and enzymes have been

inactivated, biochemical deteriorations can occur in foods, with the rates depending upon temperature and moisture content. Usually, the higher the temperature and the higher the moisture concentration, the more rapid the reaction, but reactions can occur even at temperatures below freezing and at moisture contents as low as 0.1%. Among the types of deteriorative biochemical oxidative reactions that can occur are lipid oxidation, vitamin B and C oxidations, non-enzymatic browning and flavor oxidations. Thus, in products that are otherwise biologically stabilized for ambient temperature distribution as in thermally processed foods, oxygen can play a role in further quality losses even leading to unacceptable products.

3. Measures to Exclude Oxygen

Recognition of the costs of the presence of oxygen has led to a wide array of technologies and mechanisms to effectively preclude oxygen:

1. Hermetic packaging in gas barrier package structures
2. Process and hermetically package under vacuum, e.g., cured meats, roasted and ground coffee
3. Package under inert gas such as nitrogen, e.g., instant coffee, unit portion aseptically packaged apple sauce
4. De-aerate and package, e.g., orange juice
5. Sparge with an inert gas such as nitrogen and hermetically package, e.g., instant coffee, edible oil or solid shortening
6. Blanket with inert gas such as nitrogen and hermetically package, e.g., cheese
7. De-aerate and complete processing and packaging in the absence of air, e.g., aseptic packaging of beverages on a Tetra Pak vertical form/fill/seal system
8. Apply a vacuum and tightly seal, e.g., fresh red meat, some cured meats, fresh cut produce
9. Displace the air with a reduced oxygen gas environment and tightly seal, e.g., fresh vegetables under modified atmosphere
10. Tightly seal the product and permit the contents to respire and consume the oxygen present, e.g., fresh cut vegetables, ground meat in chub packages
11. Heating to expel the air, packaging, steam injection followed by hermetic

sealing and cooling to condense the steam into water and creating a vacuum, e.g., most low acid food canning processes

12. Heating to expel the air, filling hot and hermetically sealing and cooling to condense the headspace steam vapors creating a partial vacuum, e.g., most high acid beverages and foods
13. Hot filling followed by liquid nitrogen injection and hermetic sealing, e.g., fruit and tomato juices and juice drinks in aluminum cans
14. Mechanical vacuum, e.g., cured meats and cheeses
15. Mechanical vacuum plus in-package oxygen scavenging sachets or labels, e.g., dried beef snacks and jerky
16. Blanketing or injecting with inert gas such as nitrogen plus in-package oxygen scavenging sachets, e.g., some bakery goods, bacon bits, fresh pasta, etc.
17. Addition of oxygen interceptor chemicals to the packaging material, e.g., butylated hydroxyanisole/butylated hydroxytoluene (BHA/BHT) to potato chip package materials
18. Addition of antioxidant chemical such as BHT directly to the food product, e.g., breakfast cereals
19. Addition of sulfur dioxide or analogue to the food, e.g., wine, dry fruits

In addition to the mechanisms employed to remove oxygen or obviate its effects, closure measures that are undertaken to exclude oxygen after packaging include:

1. Double seam mechanical closure with resilient liner compound to hermetically seal as impermeable metal cans
2. Crown closure for glass bottles with resilient plastic liner to seat on the glass finish for hermetic sealing
3. Long, moist cork plugs (e.g., wine)
4. Molded plastic screw closures with resilient plastic liners to seat on glass or plastic bottle finishes (e.g., carbonated beverages)
5. Roll-on aluminum closures with resilient plastic liners to seat on glass bottle finishes (e.g., beer bottles)

6. Roll-on aluminum closures with resilient plastic liners to seat on plastic bottles (e.g., carbonated beverages)
7. Screw-on metal closures with resilient plastic liners to seat on glass, bottle or jar finishes (e.g., juices)
8. Clamp-on metal closures with plastisol liners that deform under heat to the shape of the glass jar finish (e.g., baby foods)
9. Fusion heat sealing of identical plastics (e.g., retort pouches)
10. Peelable heat sealing of different plastics (e.g., aseptically packaged apple sauce in unit portion cups)
11. Mechanical clip bunching of plastic bags (e.g., fresh meat "barrier bags," chub ground meat, sausage tubes)
12. Caulking with heavy layers of flowable waxes or plastic materials (e.g., coated or laminated paperboard folding cartons)

Although mechanical oxygen removal is effective in reducing the rate of oxidative deterioration, it is a one-time action. As much as possible of the oxygen is removed in this single action, and the residual oxygen, however low, is present and available to react with the food. When present, the available residual oxygen will react with the food, usually in an adverse manner.

4. Oxygen Entry After Closure

Yet another often more serious mechanism by which oxygen is a problem with packaged food is oxygen from the air external to the packaged food entering the package by permeation through plastic materials, through can end seam compounds, or glass closure gasket compounds, or by transmission through heat seal faults and pinholes or cracks in aluminum foil. Thus, almost all hermetically sealed packages are not truly hermetic because they can permit the entry of air, which contains oxygen. This entering oxygen can continue any oxidative reactions that have been initiated from the presence of residual oxygen from the initial reduced oxygen packaging operation.

5. Historical Background

Recognition of these secondary oxygen reactions appears to have begun about forty years ago. The early research centered first about knowledge that residual oxygen was a reactant whose removal could effect superior quality retention in packaged foods. Among the materials incorporated into the food itself to reduce the

oxygen were ascorbic acid, BHA, BHT and glucose oxidase/peroxidase. These materials proved so technically effective that they were incorporated into small gas permeable flexible pouches or bags placed into the food package, initially only to remove residual oxygen, but later to intercept oxygen that entered the package. These pouches were, of course, the predecessors of current reduced iron powder sachets. The oxygen removal capacity of BHA/BHT is relatively low.

During the 1970s, concern about oxidation reactions resulting from residual and entering oxygen increased because of the greater use of plastic packaging, all of which displays some oxygen permeability, and the desire for prolonged quality retention in many packaged foods. Among the several results of these concerns was the development of new means to remove oxygen by chemical reaction using in-package packets or sachets of reactive chemicals and the beginnings of a new sub-category of packaging called active packaging.

Considerable insight into the current situation is gained by a more detailed review of the chronology of oxygen scavenger systems.

A. Early Work

As early as the 1920s, reports were published on the removal of oxygen from enclosed food components using ferrous sulfate plus a moisture-absorbing substance, copper powder and ammonium chloride, zinc and/or alkali earth metal salts. Research into methods of removing oxygen from closed packages appears to have begun in earnest with the work of Isherwood in 1943 in England based on the oxidation of ferrous sulfate. None of the very early developments appear to have been met with commercial success.

Some of the first research led to an American Can Company oxygen scavenger packaging system applied by the United States Army for dry foods, and is still often cited in historic literature. This system required packaging the product in metal cans under 8% hydrogen gas with nitrogen, which would react with residual and entering oxygen at palladium catalyst sites on the interior of the can lid.

An application to flexible pouches occurred when the company's research demonstrated that the reaction of H_2 with O_2 could be achieved by sandwiching a palladium catalyst in a plastic barrier lamination, in one case with alumina as the support and with a desiccant. In another variation, the need to gas flush was avoided by employing calcium hydride to produce H_2 on reaction with water vapor from the food; the catalyst and the hydride were in a gas permeable sachet enclosed within the package. However technically effective this system was, the concept of packaging with hydrogen had hazards, and so the system did not become a commercial success.

Oxygen absorbers using dithionite (sodium hyposulfite and hydrosulfite) as their main component were marketed in Japan in 1969, but were never widely accepted because they lacked stability during handling and storage and had some undesirable side reactions. A patent was later issued on this process on an improved system involving dithionite, calcium hydroxide activated, carbon and water.

B. 1970s

The first major commercial oxygen scavengers, as the active packaging oxygen reacting systems came to be called, were from Mitsubishi Gas Chemical Co. in Japan. During the 1970s, this company introduced reduced iron salts into oxygen permeable sachets that were placed in food packages. Any oxygen within or entering the package oxidized the iron to the ferric state in the presence of moisture drawn from the food product. Under the trade name, "Ageless®," Mitsubishi Gas Chemical oxygen scavenger packets were commercialized in Japan and introduced into the United States during the late 1970s. These systems were soon followed into the commercial market by Japan's Toppan Printing Company with ascorbic acid-based oxygen scavenger systems.

Since then, more than a dozen Japanese companies have been actively promoting the use of sachets of readily oxidized materials as oxygen scavengers for use in flexible and other packages. It has been claimed that the package internal O₂ concentration can be lowered to below 0.0001% with oxygen absorbers when appropriate scavenging materials and barrier package structures are used. Gas flush and analogous physical methods to achieve and maintain O₂ levels below 0.5% have not proven economical. These Ageless® sachets and their iron and non-ferrous analogues have been the basis for many package materials containing oxygen scavengers now under development.

C. 1980s

During the 1960s and 1970s, the technology of oxygen removal included the incorporation of antioxidants into package materials. Such compounds as propyl gallate or butylated hydroxyanisole in carriers were blended into thermoplastics ostensibly to reduce the rate of oxygen permeation through gas barrier plastic materials such as films or semi-rigid cups, tubs and trays. Among the sources for these concepts were W.R. Grace & Co. and the noted plastics' innovator, Emery Valyi, whose focus was upon multilayer barrier plastic cups. It is possible that Dr. Valyi's efforts resulted in prototype packages but no literature reference or recollection indicates reduction to commercial practice.

During the 1970s and 1980s, research on incorporating sulfites into package materials came from bag-in-box systems' developer/manufacturer Scholle Corporation and from American National Can Co. The former was directed towards incorporation of

the sulfites into multilayer flexible package materials for the explicit purpose of removing oxygen from the interior of the package. The latter were aimed mainly at removing oxygen from the interior of semi-rigid multilayer plastic retort cans often called buckets. As a major producer of buckets containing moisture-sensitive ethylene vinyl alcohol as the principal oxygen barrier, American National Can has pioneered in incorporating a desiccant layer into their multilayer plastic structure. The next step was to supplement the desiccant with an oxygen scavenger which, in this instance, came from the sulfite group. This concept was not employed in commercial practice for reasons not disclosed.

Since about 1980, Commonwealth Scientific Industrial Research Organization (CSIRO) near Sydney, Australia, has been developing systems based on the reactions of singlet oxygen. The polymer film is utilized as both a solvent for O_2 and a reaction medium for the scavenging reaction. The technique involves polymer films containing a photosensitizing dye and a singlet oxygen acceptor. On illumination of the film with visible light, excited dye molecules convert O_2 diffusing into the film from the external environment to singlet oxygen. The singlet oxygen molecules diffuse to react with the acceptor and so are consumed. The process continues as long as the film is illuminated and acceptor is available. Although an advantage of this type of system is that it requires no addition of sachets to the food package, a major disadvantage is that the reaction does not occur in the dark.

CSIRO continues to be one of the leaders in developing oxygen scavenging package materials although to date, despite the considerable investment, nothing commercial has resulted.

Advanced Oxygen Technologies (AOT), then Aquanautics Corp. in the United States, incorporated oxygen-binding organo-metallic ligand compounds into the plastic liner inside the bottle cap of beverage and particularly beer containers. The oxygen in the headspace of the glass bottle is removed by the compound, thus prolonging the shelf life of the product. This technology has been commercialized by American bottle closure producer Zapata and adopted by many boutique breweries, but not by any of the top four brewers for a flagship product. AOT's research began from a U.S. Navy program to create an artificial gill for underwater activities. In mid-1994, AOT ceased activity because of a lack of sufficient income and funding. They are currently seeking means to continue operations or to discontinue totally. Other of their proposed applications include O_2 absorbing spots, lines or coatings on the walls and/or lids of cans and polymer blends for the flexible packaging of solid foods. At present, their markets include Zapata for closure liners and Scholle for dispensing fittings for bag-in-box applications.

In another approach, England's Metal Box (then CMB, and now Carnaud MetalBox) developed Oxbar™ which incorporated the active ingredients (MXD6 nylon and a cobalt

salt which catalyzes the reaction of O₂ with the nylon) into the wall of a semi-rigid polyester bottle and prevents O₂ ingress into the container as well as scavenging O₂ from inside the container. This system was abandoned by Carnaud MetalBox in 1992 for both economic and regulatory reasons (described later in this paper in section 13 C), but evidently the technology has been acquired by an American company that since has been actively developing the system.

The use of enzymes to scavenge oxygen has been known for many years, having been suggested in the early 1900s. In 1956, patents were issued for sachets containing glucose oxidase/catalase enzymes and also a glucose oxidase treated cellophane film. Trials were conducted with a glucose oxidase sachet system referred to as "OxyBan" but it appears not to have been used commercially. In 1989, the Pharmalac entrepreneurial development company reported on an interactive package incorporating these two enzymes to remove O₂ but this also has not been commercialized.

D. 1990s

In Japan in 1990, Toyo Seikan announced the incorporation of an "Oxyguard" ferrous oxygen scavenger in their package material coextrusion in which the scavenger is in the core of a film with an oxygen permeable film on the interior. The company stated that the action of the oxygen scavenger is not initiated until required.

Also in 1990, Fujimori in Japan announced the insertion of gas permeable oxygen scavenger sachets into the space between the inner and next outer layer of packaging films. Slots in the inner film permit air within the package to pass into the scavenger sachet.

In 1990, W.R. Grace in Europe announced the commercialization of their Daraform™ closure liner containing an unidentified oxygen scavenger assumed to be ascorbic acid. This material is incorporated into a closure liner cited as free of polyvinyl chloride (PVC) which is questioned as being unsafe for the environment. In 1991, Grace began marketing this liner in the United States for beverage packaging applications.

Almost simultaneously, Cryovac Division of W.R. Grace began importing and marketing Mitsubishi Gas Chemical's Ageless® reduced iron-based sachets in the United States. Cryovac staff members perceived in-package oxygen scavengers as a major advance in food packaging technology. Cryovac's efforts paralleled those of their principal, Mitsubishi Gas Chemical.

About the same time, yet another group within W.R. Grace independently initiated development of yet another oxygen scavenger technology for packaging, the

incorporation of unsaturated hydrocarbons into plastic films.

In 1991, the American company Multiform Desiccants, Inc. which had been supplying oxygen scavenger sachets announced their development of a flat manifestation of an oxygen scavenger sachet which could be affixed to the interior of a package as if it were a label, i.e., by adhesive. The surface area is large and in indirect contact with the package interior. To date, only one offshore packager in the United Kingdom is using the Multiform Desiccants oxygen scavenger label. Also in 1991, Mitsubishi Gas Chemical demonstrated an oxygen scavenger label that was very similar to that of Multiform Desiccants. To date, Mitsubishi Gas Chemical has not commercialized its oxygen scavenger label technology.

Japan's Keplon marketed their iron-based oxygen scavenger sachet products in the United States for three years through two different agents. Japan's Toppan Printing has sold their ascorbic acid-based oxygen scavenger sachets to one account directly in the United States. An American company, United Desiccants Gates, marketed Japan's Nippon Soda's iron-based oxygen scavenger products under the OxySorb name since 1990. All of these thrusts reflect a distinctly Japanese base to much of the oxygen scavenger commercialization to date.

In 1994, Multiform Desiccants indicated that they have incorporated an oxygen scavenger into an unidentified package material with commercial introduction predicted by them for 1995. Also in 1994, Toyo Seikan's technology was introduced on a developmental basis to extend the shelf life of aseptically packaged rice.

In 1994, DuPont announced the development of aldehyde scavenger technology. The premise here is that the scavenger removes the end products of food product oxidation, and so no indication of the effects of oxidation are sensed by the consumer.

6. Commercial Applications

A market search in the United States indicated the following commercial applications of oxygen scavengers:

1. Modified atmosphere packaged chilled pasta
2. Dry beef snacks (retail packs and export packs to Japan)
 - a. Beef jerky
 - b. Pemmican
3. Precooked poultry master packs (distribution pack)

4. Real bacon bits (glass jar)
5. Macadamia nuts in jars
6. Pepperoni chips (distribution pack)
7. Bulk peanuts (distribution pack)
8. Bakery goods
 - a. Specialty "health" bread
9. Regenerated collagen sausage casings (distribution package)
10. Closure liners for beer bottles (small boutique brewers)
11. A few pharmaceuticals
12. One candy

Although a small quantity of dried beef snacks containing in-package oxygen scavenger sachets is distributed in the United States, most such packages are for export to Japan.

One manufacturer of precooked poultry employs in-package oxygen scavenger sachets for its master or distribution packs containing prepackaged product. This is the only high water activity product use of oxygen scavengers in the United States.

United States' meat packer Hormel employs in-package oxygen scavenger sachets in the bottom of retail glass jars of ambient temperature, shelf stable bacon bits as well as for a flexible pouch of pepperoni sausage slices.

Kraft General Foods' DiGiorno brand fresh pasta uses modified atmosphere (MA) packaging with in-package oxygen scavenger sachets adhered to the bottom interior of their tray.

Collagen sausage casings are made from animal collagen and extruded as uniform flexible tubes to be used as natural casings mostly for small pork breakfast sausage. They are packaged using oxygen scavenger sachets. This product represents only a small fraction of the total sausage casing market.

The current market for in-package oxygen scavenger sachets in the United States has been narrow and specialized. Fewer than 100 million sachets appear to be used

annually.

In-package oxygen scavenger sachets are well known in the United States and have been tested for many applications. In fact, in several situations, in-package oxygen scavenger sachets were used commercially and later withdrawn, e.g., in cans of roasted and ground coffee and in multipacks of wine in plastic bottles.

Objections to the use of in-package oxygen scavenger sachets include cost, speed of insertion, the presence of a loose sachet in a package, safety and liability.

7. U.S. Military Applications

Outside Japan, other than producers of fresh pasta and smoked or processed meats, the U.S. military is the largest user of oxygen absorber packets to date. The military application is for shelf-stable rations. In the late 1980s, the packets were introduced into packages of water-activity controlled Meal, Ready-to-Eat (MRE) pouch bread, which can be stored and maintain its quality for three years at 27°C (80°F). In the absence of the oxygen scavenger, growth of Aspergillus and Penicillium was visible on the bread within 14 days (Powers et al., 1990). Oxygen absorber packets are now contained inside numerous shelf-stable military food products:

1. Pouch bread, MRE
2. Pound cakes, MRE (5 types)
3. Snack items, MRE (5 types)
4. Fudge brownie, MRE
5. Hamburger buns, Heat and Serve Ration
6. Shelf-stable waffles

As with the commercial applications, there are also limitations associated with the use of oxygen absorber packets in military rations. These limitations may include the potential of the packet being broken, the risk of the product manufacturer overlooking insertion in the package, or the risk of the consumer accidentally ingesting the packet.

8. Japanese Situation

It is important that any prognosis includes a complete review of in-package oxygen scavengers with a description of the activities in Japan where the greatest amount of development has been occurring. To comprehend the commercial situation relative to

in-package oxygen scavenging, it is instructive to examine the Japanese situation where, by far, the greatest commercial success has occurred.

Probably about two billion oxygen scavenger sachets are used annually in Japan led by Mitsubishi Gas Chemical with about 70% of the Japanese market. The company reports that the market for oxygen scavengers in Japan has been growing.

At least eleven Japanese companies have competed in their oxygen scavenger market (not all are now offering oxygen scavengers):

<u>Manufacturer</u>	<u>Trade Name</u>	<u>Year Entered the Market</u>
Mitsubishi Gas Chemical	Ageless	1977
Keplon	Keplon	1978
Oji Kako	Tamotsu	1979
Toppan	Freshilizer	1980
Toagosei Chemical Industry	Vitalon	1980
Nippon Soda	Secule (OxySorb in U.S.)	1980
Hakuyo	Sansoless	1980
Finetec	Sansocut	1986
Nippon Kayaku	Modulan	1987
Powdertec	Wonderkeep	1987
Ueno Seiyaku	Oxyeater	1988
Dai Nippon		1993

Most, but not all, of the scavengers in Japan are based on the reaction of ferrous iron with oxygen in the presence of moisture.

In-package sachets may be classified as **self-working** which contain moisture in sachets and which start oxygen absorption when exposed to air, and as **moisture-dependent** which contain no moisture in the sachets but extract the moisture from the in-package atmosphere. Non-iron based scavengers include catechol-based scavengers.

Table 1 indicates the types of in-package oxygen scavengers in commercial use in Japan in approximate decreasing order of commercial importance, the conditions of use and typical applications.

TABLE 1
CLASSIFICATION OF OXYGEN ABSORBERS IN JAPAN

Function	Reactant	Typical Applications	Absorption Speed	Japanese Product	Manufacturer
O ₂ V	Iron	Self-working Dry a _w <0.3 Tea, nuts	4 - 7 days	Ageless Z-PK Vitalon T	Mitsubishi Toagosei
O ₂ V	Iron	Medium a _w a _w <0.65 Dried beef	1 - 3 days	Ageless Z Keplon TS	Mitsubishi Keplon
O ₂ V	Iron	High a _w a _w >0.65 Cakes, Bakeries	0.5 days	Ageless S Secule CA	Mitsubishi Nippon Soda
O ₂ V	Iron	Frozen +3-25°C Raw fish	3 days at -25°C	Ageless SS	Mitsubishi
O ₂ V	Iron	Moisture- dependent Pastas	High a _w a _w >0.85 0.5 days	Ageless FX Vitalon LTM	Mitsubishi Toagosei

TABLE 1 (Continued)

Function	Reactant	Typical Applications		Absorption Speed	Japanese Product	Manufacturer
$O_2 \mid$ \mid \vee	Catechol	Self-working	Medium a_w $a_w < 0.65$ Nuts		Tamotsu A	Oji Kako
			High a_w $a_w > 0.65$ Cakes		Tamotsu P	Oji Kako
$O_2 \mid$ & \vee $CO_2 \mid$ \vee	Iron and calcium	Self-working	Roasted/ ground coffee	3 - 8 days	Ageless E	Mitsubishi
$O_2 \mid$ & \vee $CO_2 \wedge$ \mid	Ascorbic acid	Self-working	Medium a_w $0.3 < a_w < 0.5$ Nuts	1 - 4 days	Ageless G Toppan C	Mitsubishi Toppan
	Organic acid and iron	Moisture- dependent	High a_w $a_w > 0.85$ Cakes		Vitalon GMA	Toagosei
$O_2 \mid$ & \vee Ethanol \wedge \mid	Iron and ethanol on zeolite	Moisture- dependent	High a_w $a_w > 0.85$ Cakes		Negamold (anti-mycotic)	Toppan (?)

The major applications of oxygen scavengers in Japan are reported as follows:

1. Bakery goods, to prevent mold; e.g., soft cakes, muffins, bread, English muffins, biscuits (including chocolate-coated), pizza and cheesecake
2. Dry snacks, to reduce lipid rancidity
3. Nuts
4. Chocolate-coated nuts
5. Beef jerky
6. Processed seafoods
7. Seasonings
8. Japanese dry noodles
9. Cheese
10. Aseptically packaged cooked rice
11. Seaweed flakes
12. Dry pet foods
13. Ophthalmic tablets
14. Cough capsules
15. Plant growth hormone
16. Antibiotics
17. Chestnuts
18. Anti-lice carpet powder
19. Natural beta carotene
20. Vitamin pills/tablets

21. Medical kits to preserve reagents

22. Kidney dialysis kits

In-package oxygen scavenging is used in a broad diversity of applications, none of which is large by itself. There are no mainstream applications in which all products within the category employs a scavenger product. In Japan, in-package oxygen scavenger sachets are specialty components used in special circumstances to meet unique Japanese requirements.

Many of the product applications are in circumstances in which the product is distributed in extra packaging since it is intended as a gift. The turnover is therefore slow, and the time in distribution is relatively long. Thus, there is a need for a means to prolong quality retention.

The commercial situation in Japan also explains the apparent fact that the overwhelming proportion of oxygen scavenging research and development has been in Japan.

As indicated previously, the apparent dominance of Japanese sources in technological development must be acknowledged and considered. Nevertheless, the primary thrust of this study was to identify United States' sources, with secondary attention to offshore technology.

CRITICAL ANALYSIS OF OXYGEN SCAVENGER SYSTEMS

1. Definitions

The terms antioxidants, interceptors, absorbers and scavengers have been used to describe the materials employed in the role of removing or preventing oxygen from entering the in-package environment of food products subject to undesirable oxidative reactions. Precision in definitions of these materials would be helpful in assessing the effectiveness of the materials, if indeed there are differences. An examination of secondary sources did not demonstrate any unanimity of definitions. In fact, many of the terms appear to be used interchangeably.

For purposes of this report, each of the commonly-used terms is assigned a definition, accepting the fact that professionals will debate these interpretations. It is also probable that these definitions will not necessarily have clear boundaries, i.e., they will overlap.

A. Antioxidants: Antioxidants are generally compounds that react with oxygen and are themselves oxidized to generate innocuous non-toxic compounds. Antioxidants are usually incorporated into the product itself as contrasted to being part of a package material system. For many years, antioxidants were, and still are, fat-soluble compounds incorporated into fatty foods to preferentially react with oxygen in the surrounding air or dissolved or occluded in the food product. In more recent years, the term antioxidant has been used more broadly to encompass compounds that react in non-lipid environments such as water-based, e.g., human body cells. The classical lipid antioxidants include such compounds as:

BHA—butylated hydroxyanisole
BHT—butylated hydroxytoluene
PG—propyl gallate

all of which are often blended with lipids to retard their oxidation. The BHA/BHT compounds are also often incorporated into polyolefin package films to retard the oxidation of the plastic materials. Yet another application is incorporation into flexible package materials for intentional diffusion to the surface, sublimation into the in-package environment and subsequent incorporation into dry food products such as breakfast cereals where the actual antioxidant effect takes place. Among the limitations of such systems is that they act only against lipid oxidation, i.e., they have no or little action in moist environments. Further, they are slow and the reactions are so limited that very large quantities are required to function as effective oxidants.

A more recent addition to the list on package material antioxidants is beta carotene.

This vitamin A precursor is being claimed to be useful in retarding oxidation in polyolefins. No claims have been made to date on their ability to reduce the passage of oxygen into the packages or to remove oxygen from the interiors of packages.

Among the other products classified as antioxidants for incorporation into package structures are ascorbic acid and its analogues. Such compounds are water soluble and effective in moist environments. In many products, ascorbic acid is called an oxygen interceptor. In the context of packaging, ascorbic acid is usually classified as an oxygen scavenger.

B. Interceptors: This interesting word describes any compound that actually blocks the adverse effect of oxygen in the air on the food usually outside the product/package, before the oxygen can enter. Interceptor has been applied to compounds in both the product and package materials. Often the word interceptor has been used in food label descriptors to avoid statements about antioxidants which, in the past, sometimes conveyed images of undesirable chemical reactions to some consumers.

Interceptors prevent oxygen from reaching the food product by themselves being oxidized before the oxygen reacts with the food product. Interceptors may be regarded as synonymous with antioxidants.

C. Absorbers: Technically absorbers remove oxygen by physically trapping the oxygen and not through chemical reaction. In practice, however, there are very few, if any, materials that can effectively remove oxygen by physical as contrasted to chemical reaction. It appears that the word absorbers is used loosely to describe any system that removes oxygen from the environment and thus delays or prevents oxidation reactions in the food product.

D. Scavengers: This is a relatively new terminology having been applied to materials incorporated into package structures to remove oxygen from the inner package environment and thus, in turn, from the food product itself through partial pressure actions. In effect, scavengers are antioxidants.

One implication that might be derived from this list of definitions is that scavengers are fast-acting, high capacity oxygen interceptors capable of eliminating large volumes of oxygen and continuing their action indefinitely as long as the scavenger is present.

The most widely known or proposed commercial oxygen scavengers are ferrous compounds, catechol, ascorbic acid and its analogues, ligands and oxidative enzymes such as glucose oxidase.

2. Antioxidants

Traditional antioxidants applied to delay lipid oxidation have been incorporated into packaging materials for many years. In recent years, Rho et al. (1986) showed that coating the interior surface of a polyethylene film package with TBHQ (t-butylhydroquinone) extended the shelf life of contained deep-fried noodles. Israel's Miltz and his co-workers (1988) demonstrated that when BHT was incorporated into high density polyethylene film, it increased the shelf life of a contained oat cereal. These researchers asserted that the applications of the antioxidants into the plastic film were more effective than adding the same antioxidant directly into the contained food products.

A 1969 patent assigned to W.R. Grace & Company, an early and still prominent participant in oxygen scavenging package material structures, describes the incorporation of lipid antioxidant n-propyl gallate into both flexible and thermoformable plastic package materials. The development was for polyolefins such as polyethylene and polypropylene and especially for polyvinylidene chloride (PVDC) (saran) film. The antioxidant could be incorporated into two-ply or three-ply structures. An example would be two layers of PVDC sandwiching the antioxidant. Also cited as antioxidants were BHA, BHT and dihydroguairesic acid, among others, with the preference being for n-propyl gallate.

The antioxidants were incorporated on the interior surface of the film from a liquid solution in which the solvent was propylene glycol, glycerol or edible oil. The antioxidant in the solvent was trapped between the two film layers. A mechanism to fabricate the material was to extrude the polymer downward through an annular die to form tubing passing through a cold water bath, reheating and blowing a bubble. A pair of nip rolls adjacent to the bath containing the antioxidant metered the antioxidant deposition into a very thin layer on the contact surface of the flexible package material. The tubing was wound on a roll to form a two-ply double wound film with the antioxidant/solvent mixture at a concentration of about 1-30 mg/ft.² concentration between the layers. This structure was intended to reduce the oxygen permeability of the film by a factor of up to six times. Product contents for the films included cheese. No mention was made of scavenging oxygen from the package interior, but it must be assumed that such a reaction occurs. We could find no commercialization of this patent within W.R. Grace & Co.

This patent is one of the very few citing conventional antioxidants and among the earliest publications describing the incorporation of antioxidants into a multilayer film structure, as opposed to into a sachet. Because of the liquid coat, it is not unlike the later (1977) Scholle patent, but the Grace patent indicates the layer is very thin and not really in liquid form.

We postulate that the type and quantity of compound proposed is insufficient to function as a long term ambient temperature oxygen scavenger. On the other hand, the mechanism for applying the active compound might have merit for other more reactive oxygen absorbers.

Valyi's patent indicated the employment of a "getter" as the antioxidant in a semi-rigid multilayer barrier plastic cup structure (Valyi, 1977). The term "getter" was occasionally used during the 1970s and 1980s to describe a material capable of binding, absorbing or adsorbing unwanted liquid or gaseous materials. Antioxidants would represent a subcategory of getters. Valyi suggested a multilayer structure of improved oxygen barrier performance as a consequence of the multiple materials functioning together. The layers proposed include an exterior high barrier plastic and an interior lower gas barrier plastic with the getter uniformly dispersed within or between the two layers. Bonding was by adhesive or electrostatic means. The objective was to reduce oxygen permeability of the total structure. The antioxidant getters cited included BHA and propyl gallate. No mechanism for dispersing the getter was described.

Valyi's innovation, highly publicized at the time, focused primarily on thermoformable multilayer barrier plastics with separable components, i.e., avoiding the use of coextrusion to achieve the structure. Thus, the "getter" was really a very minor constituent and so this was a secondary issue.

Although considerable development was involved, only a very few actual commercial packages emerged largely in the wide-mouth small jar category, but not containing a getter. To our knowledge, no commercial use is presently being made of this technology. The absence of any viable means of applying the getter suggests no special value to this patent in our context.

3. Sulfites

Sulfites and their analogues have been employed as antioxidants for many decades.

A very early Carnation Co. patent (U.S. 2,825,651) described the use of sulfite salt with copper sulfate as a catalyst for oxygen scavenging. The sodium sulfite and its adjunct pelletized powders were placed in a separate sachet. The mix removed 8.5 cc of oxygen in 5 hours.

If spread into a film, the particles can react without the presence of water because of their intimate contact with the food. In addition, since they can be ground to a fairly fine particle size, they should be able to be incorporated into a film. Yoshikawa et al. (1977) showed that a similar sulfite based scavenger system could remove 13 cc of oxygen in 10 hours. The promoters can be metals other than copper including tin, lead,

chromium, nickel, cobalt, palladium and platinum. Their patent claimed uses for prevention of oxidation of fats and oils, dried foods, raw and fresh foods of all categories and pharmaceuticals. The claims were for composition of the scavenger and not for the method of employment, and so indicates no extension directly into package materials.

In 1965, proposals were made to introduce bisulfites into in-package sachets to consume free oxygen and thus scavenge (the term was used in the reference) oxygen from packages of dehydrated eggs, dehydrated whole milk, dehydrated potatoes, edible fats and oils, and nuts (Bloch, 1965). The compound proposed was sodium bisulfite. One molecule of the bisulfite consumes an atom of oxygen forming a bisulfate. Metabisulfites were also proposed as alternatives to the sulfites.

By itself, a bisulfite does not absorb oxygen to a great extent, and so the surface area of the bisulfite was effectively increased by incorporation into a carrier with large surface area such as activated carbon or silica gel. To further increase the effectiveness of the bisulfite, a heavy metal activator was proposed with iron salts such as ferrous sulfates, ferric sulfates and chlorides preferred by the developer. Other activators suggested include hydrogen or sodium peroxide which would, of course, be incompatible with packaging applications.

The scavenger could not be in physical contact with the product, and so should be in a receptacle through which the gases can diffuse, with typical receptacles cited being bags fabricated from porous paper or cloth window. Oxygen removal is not instantaneous but is rapid at the outset, decreasing as the amount of residual oxygen is decreased. Bloch's work was performed as part of a United States Department of Agriculture program. No indication of the commercial application of the technology has been found.

In 1977, William Scholle, head of the Scholle Corporation, the world's largest manufacturer of bag-in-box packaging systems for fluid contents, received a patent on a multiwall flexible pouch material containing a sulfite compound to react with oxygen. In this situation, the sulfite is incorporated into the package in a somewhat unique fashion: the sulfite is in the form of a liquid trapped between sheets of flexible package materials. The fluid itself may be sulfite, bisulfite, metabisulfite or hydrosulfite at about 30% level in water with a citric acid buffer. The inner ply of the package structure is not intended to pass oxygen and thus remove headspace oxygen. Further, although the exterior ply has low oxygen permeability, the liquid core is intended to react with any oxygen entering from the outside environment and thus prevents it from entering the package interior.

In addition to the oxygen scavenging capability of the package material structure, sulfur dioxide gas evolved from the sulfite compounds function as microbial agents and

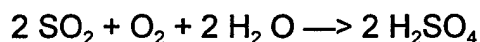
thus reduce the probability of microbiological growth and spoilage.

The package is intended for use for packaging liquids such as wine, tomato paste and tomato ketchup, but this concept is not yet being commercially employed.

Any oxygen scavenger producing an end product compound such as sulfur dioxide must be viewed with some concern since residuals of this compound can exert an allergic effect on a small population minority. Sulfur dioxide is accepted by regulatory authorities for only a relatively few food products, which must be designated as such.

The concept of introducing a liquid into a pouch requires a 100% positive seal on the package material structure and further renders the pouch vulnerable to serious adverse effects from puncture or impact.

The United Kingdom's Metal Box was granted a patent in 1980 for the use of sodium metabisulfite plus sodium carbonate in a wine bottle bung or cork, in order to release sulfur dioxide to function as an oxygen scavenger (Throp, 1980). The cork or bung was formed from molding ethylene vinyl acetate (EVA) copolymer by an injection molding process in which sulfur dioxide, carbon dioxide and water vapor are produced to fill voids within the EVA material. This residual SO₂ and water vapor trapped in the voids react with entering oxygen:



As with other references to the use of sulfites as oxygen scavengers, comments were made on the ability of the sulfur dioxide to suppress the growth of microorganisms. The patent also indicates that the sulfuric acid and sulfurous acid formed are "natural components" of wine and so their presence would actually be "highly desirable."

The most interesting aspect of this patent is the notion of incorporating the oxygen scavenger into the plastic resin before forming it and having the oxygen scavenger actuate as a result of the energy of the forming process. Because the scavenger is a sulfite, however, broad application for food packaging should not be anticipated.

Dr. Boh Tsai and his associates at American Can Company received patents on the incorporation of sulfite oxygen scavengers into plastic structures (Farrell et al., 1987). Dr. Tsai's American Can patents were clearly aimed at the company's multilayer retortable barrier plastic cans often referred to as buckets. In such cans as fabricated by American Can Co. and its successor company, American National Can Co., the multiple layers of polypropylene, ethylene vinyl alcohol copolymer as the oxygen barrier, tie or adhesive layers, are coinjection blow molded into the requisite bowl shape. American National Can also includes a desiccant layer, i.e., a layer of plastic

containing a desiccant to preferentially absorb water vapor that would otherwise interfere with the oxygen scavenging capabilities of the moisture-sensitive ethylene vinyl alcohol.

Dr. Tsai indicated that actuating the oxygen scavenger is important. In prior developments of oxygen scavenging packages, without complete protection the scavenger would react directly with oxygen in the air and thus be ineffective. In this concept, the moisture that passes from the product into the package material during processing is the triggering agent.

The scavenger listed in the American Can patent is potassium sulfite, which is a deliquescent salt that reacts only in its wet state with oxygen. The potassium sulfite may be used by itself or in conjunction with other deliquescent salts which may be actuated at lower relative humidities. Potassium sulfite is cited as an oxygen scavenger that can be readily triggered by the moist high temperature of the retorting process but has enough thermal stability to pass unchanged through thermoplastic processes such as injection molding.

In general, types of packages consist of inner and outer layers of polyolefins, typically polypropylene, tied to a core ethylene vinyl alcohol layer. The potassium sulfite could be a dispersion in a high density polyethylene carrier placed next to the inner polyolefin material.

Although aimed at retortable cans, trays and tubs fabricated from a total semi-rigid plastic structure, nothing in the concept would preclude a flexible package material (potentially for retorted products).

Dr. Tsai has joined Amoco Chemical Company which has been developing a system to incorporate an undisclosed oxygen scavenger into plastic package materials.

Australia's Commonwealth Scientific and Industrial Research Organization (CSIRO) has been in the forefront of oxygen scavenging package materials for several years. In 1994 (Steele et al., 1994), an international patent application from CSIRO described single or multilayer polymeric package films containing compounds which together can generate sulfur dioxide gas. The intent here is for the sulfur dioxide to function as a microbicidal agent for contained fresh fruits. As with previous developments, the active agents are sulfites and bisulfites coupled with hygroscopic compounds and acids which are incorporated into the package material in the dry powder form. A differentiating aspect of this concept is the use of polymers that release acid such as polylactic acid, neoprene, polyglycolic acid, etc. The final film is a multilayer lamination in which one of the layers is a conventional plastic such as polyolefin, polyvinyl chloride, etc.

No mention was made of the effectiveness of the emitted sulfur dioxide in reducing

oxygen, probably because it is essential to avoid anaerobic conditions within packages of respiring fresh produce. This is one reason that low gas barrier plastics are laminations.

A 1993 patent assigned to W.R. Grace (Hofeldt et al.) discusses the use of isoascorbates plus sulfites as oxygen scavengers in the plastic gasket liners of bottle closures. The concept in this patent was to remove oxygen from the headspace of glass or even plastic bottles and to significantly reduce or even eliminate the quantity of oxygen otherwise permeating through the liner compound. Since the primary oxygen scavenger discussed is isoascorbate, this development is reviewed below under ascorbic acid and its analogues. Sulfites are cited as one of several oxygen scavenger systems that could be incorporated into the closure liner, with no elaboration. Tannins, also indicated by Mitsubishi Gas Chemical as catalysts in the 1-2 glycol development, are indicated in this patent with no elaboration.

Perhaps the interesting relevance of this patent is the notion of direct incorporation of the dry oxygen scavenger in a thermoplastic material.

4. Boron

A 1992 Mitsubishi Gas Chemical patent (Sugihara et al., 1992) describes an oxygen absorber that overcomes the problem of triggering metal detectors on packaging lines which occurs with iron compounds. The oxygen absorber is a reducing boron and an alkaline compound plus a carrier, all contained in an in-package sachet. Suggested absorbers are boron itself, boric acid and salts of boric acid plus alkaline compounds such as sodium carbonate. The proposed carriers are activated carbon and diatomaceous earth. The dry materials are blended and packed in a sachet for placement in a package. The inventors indicate effectiveness in packages of food such as rice. Oxygen concentration within a package could be reduced from the 20.9% in air to less than 0.1% in three days. Their tests indicated that the sachet contents could not be detected in a metal detector. Although mention was made of the applicability of the invention to help prevent corrosion of metal and electronic products, no indication was given of how the boron/alkaline/activated carbon, might be incorporated into a package material. The patent therefore suggests yet another chemical that might be employed as an oxygen scavenger.

5. Glycols and Sugar Alcohols

Another patent from Mitsubishi Gas Chemical (Sugihara et al., 1993) proposes a range of non-ferrous compounds in the role of oxygen absorbers:

- 1,2 glycol such as ethylene or propylene glycol (preferred), alkaline substance and a transition metal compound such as iron, cobalt or nickel halides, sulfates

- 1,2 glycol, alkaline substance and a phenolic such as catechol or tannic acid or quinone such as benzoquinone compound functioning as a catalyst
- glycerine and an alkaline substance
- sugar alcohol such as sorbitol, xylitol or mannitol and an alkaline substance

These materials, also used to avoid the use of metals that might trigger metal detectors, are blended and placed in gas permeable sachets to be inserted into high gas barrier packages. Among the products packaged using this oxygen scavenger system are brown rice and jam-filled sweet soft bakery goods. Neither speed nor capacity of absorption was great compared with alternative scavengers. No indication of the incorporation of the scavenger directly into the package material was made. The significance of this patent is in the identification of 1,2 glycols and particularly propylene glycol, and sugar alcohols such as sorbitol and mannitol as oxygen absorbers. It is interesting to note that propylene glycol has been used as a plasticizer in cellophane sheet.

6. Unsaturated Fatty Acids and Hydrocarbons

In 1978, American pharmaceutical company E. R. Squibb was granted a patent on the use of drying oils such as linseed oil as an oxygen absorber in a gas permeable "package." The highly unsaturated glyceride was soaked into a porous plastic sponge which was in turn placed within a protective gas permeable capsule into which air could flow. A quantity of linseed oil ranging from 0.002 to 0.02 cc per cc of air was indicated as sufficient to react with all the oxygen within the container, generally bottles or preformed plastic blisters with heat sealed aluminum foil closures. No information on the effect of odorous end products of drying oil oxidation on the contained food was published. To our knowledge, no commercial application of this concept was made by Squibb. As indicated below, however, Japan's Mitsubishi Gas Chemical adopted the concept into several of its sachet scavenger patents.

Focusing on oxygen absorption from within packages of products such as metals or electronic parts subject to corrosion, or photographs if exposed to moisture, a 1994 Mitsubishi Gas Chemical patent (Inoue et al., 1994) describes the use of unsaturated fatty acids or unsaturated linear hydrocarbons as the oxygen reactants. Such compounds are described as having "remarkably high oxygen absorption capability" over prolonged periods. As in so many other of Mitsubishi Gas Chemical's developments, the oxygen scavengers are placed in gas permeable sachets which in turn are within the low gas permeability food package. The authors detail the construction of the bag (sachet) containing the oxygen absorbent material and also identify the preferred components of the oxygen absorbents. Hydrocarbons such as isoprene, butadiene and squalene are indicated. Unsaturated "fatty acids" are actually

soybean oil. Catalysts such as iron and cobalt salts may be incorporated and carriers such as activated carbon and zeolite are employed. Data presented indicate that the times needed to attain a 0.1% oxygen concentration are in the 9 to 15 hours range. The absorbers are capable of continuing their activity at least through 74 days evidently at ambient temperature. No indication was given on the oxidation of unsaturated fatty acids which are, of course, generally malodorous. Not clear was any complementary effect of unsaturated hydrocarbons and unsaturated fatty acids, nor why many of the combinations included both classes of compounds.

The origins of the use of unsaturated fatty acids and their analogues for Mitsubishi Gas Chemical were expressed in an earlier patent covering the oxygen absorbent itself (Inoue et al., 1990). The compounds cited are unsaturated fatty acids and their analogues such as oleic, linoleic and linolenic and arachidonic acids, contained in oils such as linseed and tung. Transition salts of metals such as iron, cobalt and nickel were suggested to accelerate the oxidation, with iron preferred. The unsaturated fatty acid is blended with a basic substance such as carbonates or bicarbonates which capture the unpleasantly odorous compounds formed by the reaction between the fatty acid and oxygen. Concentration of oxygen within a pouch could be reduced to less than 0.1% within 24 hours by a mixture of about one gram of the fatty acid plus 0.1-0.2 grams each of an iron compound and a basic substance. The Mitsubishi Gas Chemical developers suggest using the unsaturated fatty acid blend in sachets within packages of product.

Another of the several developments suggesting the application of unsaturated linear hydrocarbons is in an international patent application assigned to W.R. Grace & Co. (Speer et al., 1994). The invention is intended for use in bottle closure liners and also in coextruded films, preferably for refrigerated foods at lower temperatures, especially below 10°C. Since the invention's primary objective is flexible films and not bottle closure liners, this report discusses the film application.

The oxygen absorber is an ethylenically substituted or unsubstituted hydrocarbon. An unsubstituted ethylenically unsaturated hydrocarbon has at least one aliphatic carbon:carbon double bond and is exclusively carbon plus hydrogen. A substituted compound has a double bond but is less than 100% carbon plus hydrogen. The preferred hydrocarbons have three or more unsaturated groups. Among the unsubstituted hydrocarbons cited include isoprene, butadiene, styrene butadiene, oligomers such as squalene and even beta-carotene. The preferred substituted hydrocarbons include esters, carboxylic acids, aldehydes, ketones and unsaturated fatty acids.

For making transparent oxygen scavenging film layers, 1,2-polybutadiene is preferred particularly because it can process like polyethylene and because it retains its transparency and physical properties even after almost all of its oxygen capacity has

been consumed. Further, it has a relatively high oxygen capacity and a relatively high oxygen scavenging rate, especially at the lower temperatures because of its low glass transition temperature.

As is apparently required of most higher molecular weight oxygen scavengers, a transition metal catalyst such as iron, cobalt or nickel, with cobalt preferred, is required in the form of 2-ethylhexanoate or neodecanoate. The metal salt may also be incorporated directly into an ionomer, such as DuPont's Surlyn® ionomer.

The scavenging compounds are blended with what are referred to as diluents that are thermoplastics such as polyester, polyethylene, polypropylene, polystyrene, ethylene vinyl and acetate, i.e., all the common packaging thermoplastics. The components are blended using common plastic resin compounding procedures. Films may be fabricated by most of the common plastics fabrication procedures such as coextrusion, solvent casting, and/or extrusion coating; and more rigid containers by injection molding and/or stretch blow molding.

Scavenger compounds are incorporated in the range of less than 5% of the total weight of the package material. The finished plastic may be semi-rigid as in sheet for thermoformed trays, tubs and cups, or as in extrusion or injection blow molded bottles.

A typical multilayer film described is an outer low oxygen permeability layer (1-10 cc O₂/m²/day at 25°C)/oxygen scavenging layer/inner high gas permeability layer. Multilayer flexible film structures may be prepared by coextrusion, coating or lamination.

The published patent application suggests an oxygen scavenging rate of 0.5 cc per gram of scavenger per day at ambient temperature, with capability of even greater than 5 cc per gram per day. In actual application, the oxygen scavenger is capable of establishing an oxygen level of less than 0.1% in less than four weeks, but evidently faster rates can be achieved.

Among the examples cited was a multilayer blown coextruded 0.003 inch film consisting of 0.001-0.0015 inch ethylene vinyl acetate and a second layer of 90% syndiotactic 1,2-polybutadiene plus the cobalt neodecanoate and an benzophenone photo-initiator. The film is capable of scavenging oxygen at a rate of 450 cc per square meter per day at room temperature.

The development described is continuing with most of the closure liner work being performed in the United Kingdom. Grace staff have stated that this development is several years away from being commercial but thought that they would very much like to work with U.S. Army Natick R,D&E Center on the subject. Major issues in this confidential proprietary development cited include both processing and regulatory obstacles.

7. Palladium Catalysts

The noted American Can Co. palladium catalyst/hydrogen gas oxygen scavenging technology may have been derived from two earlier patents assigned to Universal Oil in 1969 (Quesada, 1969). In these patents, the palladium catalyst was dispersed on alumina, i.e., porous aluminum oxide, and dried. Up to 0.5% palladium catalysts per weight of aluminum was employed. The catalyst may be within a sachet in the sealed food package, or incorporated into the interior package walls in the ratio of up to two grams per 15 cubic inch container. The headspace gas is a blend containing up to 5% hydrogen and the balance nitrogen. Since the patents focused on the catalyst system, only vague references to the application system were published.

American Can Co.'s version was a flexible material named Miraflex 7™ (Zimmerman et al., 1974). The developers noted that the scavenging reaction produced water which had to be trapped or removed since the contents were usually dry. Oxygen concentrations as low as 0.001% could be maintained over a six month time frame. According to Labuza and Breene (1989), the price of this material was 30 times that of aluminum foil.

A 1981 patent assigned to Ethyl Corporation (King, 1981) describes almost the same palladium catalyst as did American Can. Because of Ethyl Corporation's interest in closure liners, King reported incorporation into the liner of a bottle or jar closure. An interesting aspect of this development is the incorporation of the finely divided catalyst on aluminum oxide carrier which is then blended into polyolefins or waxes cited as oxygen permeable. This layer is separated from the jar interior by an oxygen permeable ionomer layer. Above the reactants in the closure is a moisture absorbing or desiccant layer. This concept might, of course, be converted into a film. Ethyl Corporation is no longer a package material supplier; this part of their business was acquired by Tredegar Industries.

8. Enzymes

Enzymes are biological catalysts which accelerate chemical reactions but are not consumed as a result of the reactions. Within limits, for as long as active reactants and water are present, enzymes will function to catalyze reactions. When the proper enzymes are introduced under the proper conditions, they are capable of catalyzing desirable reactions. Enzymes therefore are very specific in their ability to catalyze reactions.

The kinetics of enzyme reactions are obviously of great importance in considering their potential commercial applications. At the outset, enzymatic reaction rates are linear with time until all of the free enzyme is consumed to form the enzyme-substrate complex. When all of the enzyme exists as enzyme-substrate complex, or as soon as

the oxygen reaction end product is formed, the enzyme reacts with another reactant or substrate molecule, and the rate of conversion of reactant to product plateaus at the maximum reaction rate or velocity. Once the initial velocity has been achieved, all of the enzyme exists as the enzyme-substrate complex.

For in-package situations, the enzyme may be added directly to the product to effect a reaction, or it may be incorporated into the package structure. To function within a package material, the enzyme must be immobilized and the substrate, reactant or a constituent must be circulated past the site to effect a reaction. Immobilization of an enzyme, or placing it in a static position where it may function for an indefinite period, may be accomplished by making the enzyme an integral part of the packaging material.

Active packaging in general often involves the incorporation of a chemical into the package material. Active packaging employing one or more enzymes involves the incorporation of the specific enzymes into the package material in much the same manner as the incorporation of a more conventional chemical. The key differences are: the enzyme is not changed by the reaction and may continue to function indefinitely; the enzyme is vulnerable to variations in temperature, pH and relative humidity; the range of environmental conditions for the enzyme's functioning is a relatively narrow band. These key considerations that affect the ability of the enzyme to function require special processes and techniques for incorporating enzymes into packaging materials. More often, harsh manufacturing processes and geometric configurations that are adequate and even appropriate for non-enzyme packaging components often disqualify the use of enzymes. Consequently, new and innovative methods are likely to be required to incorporate enzymes into packaging materials.

Although a broad range of enzymatic reactions arising from their incorporation into package materials might be conceived, only a relatively small number have actually been attempted on a practical basis. The major examples being oxygen removed by means of glucose oxidase plus catalase.

Enzymes and their roles have been known for many decades, but the notion of incorporating them into package materials to achieve a desirable result dates back only to the late 1940s. Almost simultaneously with the idea of protecting against browning of dry foods such as eggs by removing residual oxygen, the notion of in-package glucose oxidase/catalase reactions was born. In reality, the initial action of glucose oxidase is with residual quantities of glucose, a reducing sugar active in the non-enzymatic, non-oxidative Maillard browning reactions. Since highly reactive hydrogen peroxide is produced by glucose oxidase, it must be removed by catalase which breaks it into water and oxygen. This concept was reduced to practice employing porous packets of the enzyme mix in which the enzymes slowly reacted with minute quantities of residual oxygen, an analogue of the commercial incorporation of desiccant sachets to reduce

the in-package relative humidity. The applications during the 1940s and 1950s appear to have been largely confined to very long term storage of military foods.

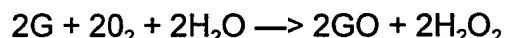
The exponential growth of modified atmosphere packaging in the 1980s led to the concepts of oxygen, carbon dioxide and moisture control using in-package sachets of chemicals, including some enzymatic agents.

Towards the end of the 1980s, interest increased with the formation of PharmaCal, Ltd. whose objective was to develop the application of enzymes in packages. Dr. John Budny, who is the sole proprietor of PharmaCal Ltd., suggested and, in some instances, physically evaluated glucose oxidase/catalase to remove oxygen which immobilized enzymes within package structures to catalyze reactions of products contained within packages. They worked with International Paper in paperboard packages, but this activity was discontinued five years ago.

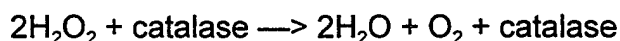
Whether or not the communications emanating from the PharmaCal Ltd.'s activity were directly responsible, several other enzymatically-based active packaging oxygen control devices have been proposed since that time.

According to Dwight Baker in 1949, the addition of an oxidase to a liquid-containing food product such as beer, peas, corn, milk, apple cider or orange juice, protected these products from oxidation. "In some instances, it is better to produce in the product a substrate for the oxidase that is to be introduced rather than to use a substrate already present." (Baker, 1949) For example, glucose originally present or added can be oxidized to gluconic acid. Baker's patent indicated that if the oxidase produced an objectionable end product such as hydrogen peroxide, then an additional enzyme might be introduced to remove the undesirable end product.

Among the interesting aspects of this early patent was the idea that as the oxygen in the product is removed, free oxygen in the headspace is further dissolved by equilibrium dynamics, thus removing oxygen from the headspace. The reaction, which is now very well known, is:



where G is the substrate. Since hydrogen peroxide is a very good oxidizing agent, it is "just as objectionable, or even more so, than is the original molecular oxygen" (Baker, 1949). Thus, catalase is introduced to break down the hydrogen peroxide:



The sum of these two reactions yields half the oxygen originally present and therefore ultimately the free oxygen approaches zero.

Baker's invention was implemented by introducing one or more pellets of the enzyme into a product, such as beer or orange juice. The patent did not explicitly describe precisely how the enzymes were incorporated. The inference was that the enzymes were introduced directly into the product. Expressed differently, this patent did not indicate that the enzymes were either part of the package structure or in an independent packet within the primary package. Thus, although the 1949 patent described the employment of enzymes to eliminate in-package oxygen, it did not indicate that the enzymes were part of the package material or structure.

This concept of enzyme incorporation into a package material was first overtly described in a 1956 patent (Sarett, 1956; Sarett, incidentally, was the assignee for the Baker patent). In this patent, the same basic enzymatic reactions as in Baker were reiterated as a reference, but the enzymes glucose oxidase and catalase in a solution were impregnated into or onto a moistureproof paper or fabric sheet. The enzyme was bound to the sheet with a water-dispersible adhesive such as polyvinyl alcohol, starch, casein or carboxymethyl cellulose. The enzyme coating face must contact the moist product to ensure that the requisite oxygen reduction reactions take place. The enzyme system was claimed to serve as a barrier to oxygen that would otherwise have been transmitted through the sheet. Products described as benefitting from this system of oxygen reduction include cheese, butter and frozen foods subject to browning.

Although during the period of the patent a Kraft packaging paper called "moistureproof" (which, it happens, was not moistureproof) was often used to package butter and cheese, the patent does not indicate the use of this material. Rather, the package material is described as having "... an exposed surface covered with a gas-permeable packaging material and having an inter layer between and in contact with packaging material and ... food ... inter layer providing an oxygen barrier" (Sarett, 1956). The specific package materials identified were moistureproof cellophane, paper, rubber hydrochloride with impregnation employed for the papers and coating for the plastic and cellulose films. Also cited as being suitable substrates were wax paper, styrene, polyethylene and vinyls.

Experiments discussed in the body of the patent indicated results in which oxidation of cheese surfaces was retarded by the presence of the enzyme-containing package material.

In 1958, Scott (co-inventor on the 1956 Sarett patent) of Fermco Laboratories, published a paper on "Enzymatic Oxygen Removal from Packaged Foods" that describes enzymes that were incorporated into packaging materials or introduced into packets. Fermco Laboratories is a manufacturer of enzymes, one category of which was labeled "Fermcozyme" antioxidants, and of the packets which were named "Oxyban". This paper marked the first publication to our knowledge on the use of packets of oxygen scavenging chemicals in packages.

The glucose oxidase/catalase systems were derived from mold mycelia which were disrupted, filtered and further purified. To be effective in reducing oxygen, glucose oxidase/catalase systems must be used in gas tight packages.

Among the applications suggested in the publication are:

1. Aqueous foods
 - a. Direct incorporation in mayonnaise or carbonated beverages
 - b. Surface treatment in canned dog food
 - c. In packets in situations in which the enzyme and the product should be kept separate
2. Non-aqueous foods
 - a. Direct incorporation
 - b. In packets, as for chow mein noodles

The mayonnaise and carbonated beverage examples involved incorporation of the enzyme system directly into the products, with oxidative rancidity delayed in the former class of products and color fading (e.g., grape flavor carbonated beverages) as well as flavor oxidations delayed in the latter. The dog food example was also a direct addition to retard surface discoloration on the top of the dog food in retorted cans.

The dried enzyme system was coated on the surfaces of package materials for process cheese. Deposition of the enzymes was in solution form or incorporation in a dry starch mixture prior to "dusting" the package material surface. When the dry and therefore inactive enzyme picked up moisture from the product, it was activated and was a sufficient oxygen interceptor to control formation of brown ring. Another series of experiments focused on obviating oxidative gray coloration on the surfaces of luncheon meats.

Fermco's Oxyban product was a dry glucose oxidase/catalase/glucose/buffers blend to be incorporated into products to reduce headspace, occluded and dissolved oxygen in dry foods such as coffee or soup. In another manifestation, the Oxyban was placed in small packets in which it reacted with oxygen in packages of roasted and ground coffee, smoked yeast or egg solids. Exactly how the enzyme was activated without moisture was not indicated, but obviously some moisture from the product was required. The author noted that this in-package packet was analogous to the desiccant packet.

Three years later, Scott, then with Hammer, elaborated on the oxygen-scavenging packet for in-package deoxygenation (Scott and Hammer, 1958). Using the same glucose oxidase/catalase packet system described earlier from their laboratory experiments, they proceeded forward to a more commercially viable mechanism. Among the issues they enumerated were: oxygen scavenger surface area, the need for moisture (cited above); necessity to neutralize gluconic acid to avoid enzyme deactivation; package material structure that will pass oxygen but not moisture.

The gluconic acid problem was obviated with phosphate buffers. As little as 15 grams of Oxyban enzyme mix in a packet was capable of removing all measurable oxygen from a sealed No. 2 size can held at ambient temperature. Once again, the type of package material used for the packet was not indicated.

An interesting side note was an exploration of the use of glucose oxidase alone that led to an increase in the amount of hydrogen peroxide, which would, in turn, slow the subsequent rate of oxygen uptake.

The products benefited by the total system were primarily dry milk, potato granules and ice cream mix.

A relatively recent international patent application from Finland (Lehtonen et al., 1991) described a package material containing an enzyme system to remove oxygen from the interior of the package by enzymatic reaction. By removing the oxygen, the growth of aerobic microorganisms was significantly retarded. This technology was favorable to shelf life from both microbiological and chemical standpoints. The enzyme, e.g., glucose oxidase, was incorporated into a package material with a gas-impermeable layer on the exterior and a gas permeable layer on the interior. The layer containing the oxygen-consuming enzyme was sandwiched between two plastic film layers.

The background of this patent cited a 1969 German publication describing the use of glucose oxidase in package materials for the surface protection of meats, fish and cheese products. The classical review paper by Labuza and Breene (1989) described a similar technology of coating plastic film with glucose oxidase catalase, with the enzyme system activated by moisture from the food.

This patent application from Cultor Ltd. Of Helsinki, Finland, details a flexible package structure containing an enzyme system in liquid phase trapped between films, the outer of which might be polyamide (nylon) or polyvinylidene chloride coated polyester. The inner film would be polyethylene which is generally not a good gas barrier.

The enzymes of choice were oxidases of the oxidoreductase family using

oxygenases and hydroxylases which bind oxygen to oxidizable molecules. The enzyme solution contains a buffer and a stabilizer, and may also be mixed with a filler. The enzyme layer was applied on the film by gravure or screen technique in a layer thickness of about 12 micrometers. The enzyme does not directly contact the food contents.

The films produced were employed either as the lidding film layer or as the thermoformable bottom layer for tray-type packages.

The inventors noted that as the temperature increases, the gas permeability of package materials increases, which also increases the ability of the enzyme system to reduce the oxygen content from the 20.9% of air to about 1% at ambient temperature within one day.

From technological and potential commercial perspectives, this Finnish work is so precise as to imply a major advance in the ability to implement the principles of enzymes as active package components.

PharmaCal, Ltd.'s claimed contribution to enzymes in active packaging was to expand the concept of packaging beyond the two, basic functions of packaging: containment of the product and protection of the contents.

PharmaCal, Ltd. added another dimension to packaging by allowing an individual package to become a processing unit, i.e., to become active. With the enzyme present, the package can perform a function that was previously limited to in-plant operations. PharmaCal developed a two-enzyme system involving glucose oxidase and catalase to intercept oxygen and applied the technology for enzymes in active packaging to improve the concept of oxygen removal. The use of the enzymes to remove oxygen was acknowledged as not new, but their role in enzyme-based active packaging has been regarded as a more advanced application. In the development, liquid packaged in a polyethylene coextrusion coated paperboard gable top carton reacted enzymatically with glucose in the package wall to form gluconate. The resulting hydrogen peroxide was enzymatically reacted with catalase to produce oxygen and water that re-enter the contained product liquid.

A 1989 patent (application) (Budny, 1989) describes a container with an internal reactor, which is really an integral section of the package wall containing the enzymes through which the liquid contents flow and to permit the enzymes to react.

Another patent (Ernst, 1991) describes a glucose/glucose oxidase enzyme mixture in a porous precipitated silica acid carrier. Calcium carbonate, calcium hydrogen phosphate, magnesium carbonate or disodium hydrogen carbonate may also be employed as carriers or reaction accelerators. The oxygen scavenger may be in the

interior of in-package sachets.

A 1991 patent (Copeland et al., 1991) describes the incorporation of oxygen scavenging cell membrane fragments that contain an electron transfer system in alcohol or acid solutions to reduce oxygen to water. The active components of membrane fragments in this technology must be the enzyme systems in the cell walls.

The inventors note that although the major mechanism to effect the reaction is incorporation of the membrane fragments into the product, these active components may also be made part of the package structure. Sources of the membrane fragments were cell membrane of bacteria such as Escherechia coli and/or mitochondrial membranes.

Examples of products from which oxygen might be removed by the system include beer, wine, fruits, juices and a variety of non-food products. Both red and white wines were treated with materials supplied by Oxyrase, Inc. which is also the patent assignee. Dissolved oxygen was removed within 16 minutes at 37°C. Less than 12 minutes was required to remove 100% of the oxygen from beer or tomato juice. A five time increase in the time to the onset of browning of banana and apple cut surfaces was observed at ambient temperature. This start-up company indicated a desire to work with U.S. Army Natick R,D&E Center in developing what is in effect a laboratory concept.

Labuza and Breene (1989) analyzed the issues of incorporating glucose oxidase into package materials. They suggested that to counteract the quantity of oxygen passing through an aluminum foil lamination, an enzyme surface will have to react with oxygen in the following manner:

$$\text{Rate} = \text{permeability} \times \text{area} \times \text{oxygen pressure difference} \\ \text{between the outside and inside}$$

$$\text{Rate} = 0.1 \times 1 [0.21 - 0.01] = 0.02 \text{ cc/day/m}^2 \\ = 20 \text{ }\mu\text{L/day}$$

This calculation above assumes air outside and less than <1% oxygen inside. For the worst case, i.e., with a pinhole or cracked score, there would be the need to scavenge 1 cc/day. A polymeric film could be made equivalent to an aluminum foil barrier by binding the oxygen scavenging enzyme to the inside surface of the film to react with the excess oxygen.

Glucose oxidase transfers two hydrogens from the -CHOH group of glucose to oxygen with the formation of glucono-delta-lactone and hydrogen peroxide. The lactone then spontaneously reacts with water to form gluconic acid. One mole of

glucose consumes one mole of oxygen. To reach zero oxygen in a package with 500 cc headspace, only 0.0043 moles of glucose are needed. The major factors are the speed of the enzyme reaction, the quantity of glucose available and the rate at which oxygen enters into the package. In the presence of catalase, a normal contaminant of commercial glucose oxidase, the hydrogen peroxide is broken down. In the presence of catalase, one glucose reacts with one-half mole of oxygen thus decreasing the overall effectiveness of the system. Pure glucose oxidase without catalase is reportedly expensive.

If no surface exists for the peroxide to diffuse, the glucose oxidase will be inactivated, precluding this application. Since many foods may have minimal contact with the package surface, except on the sides and bottom, this may not be the best approach for oxygen scavenging.

At 30-40°C, pure glucose oxidase has a rate of oxygen consumption of about 150,000 $\mu\text{L/hr/mg}$. Spreading the enzyme at a concentration of 1 mg per m^2 on a film would be equivalent to reacting all the oxygen coming through a film having a very high oxygen permeability of about 18,000 cc/day/m^2 .

Thus at room temperature, a one meter square surface with one milligram of enzyme spread out on it should be able to handle all the oxygen coming through any package film. One advantage is that both polypropylene and polyethylene are good substrates for immobilizing enzymes. Another factor is the stability of the enzyme when bound to the film. An unknown factor is how stable the enzyme remains on the film over time. Glucose oxidase bound to a plastic surface has been shown to undergo a 50% drop in activity in 2-3 weeks followed by little further loss over the next four weeks.

Some Japanese researchers have worked on binding of enzymes to chitosan, insoluble polymeric carbohydrate from shellfish shells, but a 70% loss in activity for bound glucose oxidase has been reported. Glucose oxidase that is immobilized on polyethylene-imine-coated glass beads retain 78-87% of the activity and is more stable to heat inactivation.

Since the enzyme is a protein and can serve as a nutrient for microbes along with the glucose substrate, a microbial inhibitor may be needed in the film.

The concept of glucose oxidase as an oxygen scavenger in or on a package material has been studied for many years and warrants some direct experimental demonstration to ascertain its commercial validity.

Besides glucose oxidase mentioned previously, other enzymes may have potential as an oxygen scavenger. One such enzyme is ethanol oxidase which oxidizes ethanol to acetaldehyde in an extremely rapid reaction. Hopkins et al. (1991) describes a

package in which alcohol oxidase or cellular extracts of Pichia pastoris cells containing alcohol or oxidase are the enzymes used for oxygen scavenging in dry foods. An alcohol substrate either from the product or introduced into the package from the exterior is required to remove the oxygen from the package is headspace.

9. Yeast

At least two 1980s/1990s patents dealt with the use of yeast to remove oxygen from the headspace of hermetically sealed packages. One patent from Gist Brocades, the noted Dutch enzyme manufacturer, focused on the incorporation of immobilized yeast into the liner of a bottle closure (Edens et al., 1992). The other patent, developed/written by an apparent entrepreneur, used the yeast in a pouch within the package (Nezat, 1985).

The idea is that when moistened, the yeast is activated and respire, consuming oxygen and producing carbon dioxide plus alcohol. In the bottle closure application, any carbon dioxide and alcohol produced would enter the contents, in this case beer, without causing measurable changes in the product.

The Gist Brocades venture was abandoned after considerable product and market development when it was ascertained that there was insufficient interest in the concept by major brewers. Further, of course, there was concern about recontaminating the beer with yeasts. (The use of dry yeast was reported to preclude the activation of the yeast during the thermal pasteurization process undergone by most beers.)

Yet another issue that was of consequence to Gist Brocades is the intense marketing effort that was mounted during the period when AOT directed its research and activities towards beer closure oxygen scavenging.

It is difficult to envision how this concept of immobilized yeast might be easily applied to a package film or sheet for a major primary package structure. Further, questions have been raised on the long-term effectiveness of immobilized yeast systems. Finally, and of great importance, the alcohol end product for most foods and beverages must be removed, which is not an easy task.

10. The Package Material As A Reducing Agent

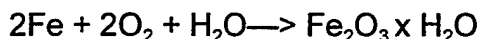
An interesting concept from Japan's Nippon Steel involves using the package itself, in this instance a metal can, as the oxygen scavenger (Maeda et al., 1989).

The inventors found that by providing a hydrophilic coating layer on the surface of a can body material, oxygen scavenging proceeds rapidly without oxidation of the base material. A hydrophilic coating and an oxygen-permeable layer are applied to function

as an oxygen scavenging system. This system may be any metal reactive with oxygen, such as iron, zinc or manganese, applied as a thin layer by vacuum deposition. Materials other than metals, such as plastic film, cellophane, paper or glass, having a thin metallic layer (0.5 to 20 mg per dm²) of the reactive metal may be applied in an adhesive vehicle to the interior of the steel can.

Ordinary steel sheets and surface-treated steel sheets conventionally used for cans, such as a tin-plated steel sheet or chrome-plated steel sheet, may be used for preparing cans or containers for foods and drinks, e.g., beer and juice. The metallic base materials may further be chemically treated with, for example, phosphates and chromates. Due to a stable oxidized layer formed on the surface, the aluminum sheet does not further react with oxygen or oxidation occurs extremely slowly. Therefore, the aluminum sheet is coated with metals such as iron, zinc or manganese with oxygen absorbing ability. The thickness of the coating needs to correspond to the quantity of oxygen contained in the packages and accordingly, the thickness varies depending upon contents and the sealing conditions.

For example, in the case of a 350 ml beer can (0.16 ml of O₂ in 24 ml of a headspace), O₂ is consumed according to the following equation when using an iron coating as an example:



$$\frac{0.16 \text{ ml} \times 4 \times 55.85 \text{ g}}{3 \times 22,400 \text{ ml}} = 0.53 \text{ mg Fe}$$

or about 0.5 mg/dm² of iron.

In the invention, there is no particular limitation with respect to the coating composition used for forming the hydrophilic coating layer that is capable of dissolving or swelling in water on the surface of the metallic base material. The preference is a solution having a solids content of approximately 0.1 to 20% by weight of water-soluble polymer used as a binder and dissolved in water. The coating is applied by ordinary means, such as spraying followed by drying. The thickness of the hydrophilic coating layer is generally in a range of 0.01 to 5 µm. The water soluble polymer used in the coating may be cellulose derivatives, such as hydroxyethyl cellulose, since they can impart an excellent oxygen absorbing ability to the base materials. The hydrophilic coating layer may be applied to the entire surface of the metallic base material or, depending upon purposes, be applied partly to, for example, the lid or the bottom of a sealed container.

If the rust formed by reaction of the metals with oxygen and water adversely affects the quality of the contents, an oxygen and moisture permeable coating layer on the

hydrophilic coating layer is employed. The coating can minimize transfer of part of the coating-forming components which impair the flavor of the contents when they contact the contents in a sealed container; or the coating can also minimize permeation of metal ions, metal oxides and metal hydroxides. Resins suggested include silicones.

A desired oxygen permeation of the oxygen and moisture-permeable coating layer can be given when a resin having a P value (oxygen permeation coefficient of a resin in the equation described above) of 10^{-9} cm/cm² seconds cm Hg or more is used. The layer having a higher oxygen permeability generally gives higher moisture permeability and by using the resin having the P value, a coating layer with sufficient moisture permeability can be obtained.

Polyolefin resins, such as polyethylene, polybutadiene and polymethylpentene are preferred from the standpoint of oxygen and moisture permeability and the feasibility of can manufacture. These resins can be applied in a film form by thermal pressure deposition or by adhesive.

An oxygen and moisture permeable layer may be coated directly on the surface of the metal or onto the hydrophilic coating layer by roll, spray or immersion coating followed by drying, or may be applied by laminating a film.

In the invention, with the hydrophilic coating layer formed on the surface of the metallic material, the reaction between the oxygen and the metal is accelerated by the presence of water. Further, with an oxygen and moisture permeable layer formed on the hydrophilic coating layer, effects of rust (iron oxide) formed can be avoided without lowering the oxygen absorbing ability.

Although aimed at metal cans, this concept appears to be applicable to other types of packages because the examples included vacuum deposition of iron on the surface of a flexible package film.

This development warrants further investigation.

11. Ferrous Iron-Based Absorbers

By far the most significant oxygen scavenger in commercial use and in development is that based on ferrous iron. This type of oxygen absorber was commercially developed by Japan's Mitsubishi Gas Chemical Co. under the trade name "Ageless" but is also available from other suppliers under other trade names.

The product is basically ferrous iron which oxides to the ferric state. The water activity of the food must be high enough to provide moisture for the iron to oxidize. A level of 0.01% (100 ppm) oxygen within closed packages is achievable.

The iron powder is separated from the food by keeping it in a small, highly oxygen-permeable sachet clearly labeled "Do not eat" because of the possible toxicity if the contents of the sachet were accidentally consumed. The LD_{50} (lethal dose that kills 50% of a population) for iron is 16g/Kg body weight. The largest sachet commercially available contains 7 grams of iron which would amount to only 0.1 g/Kg for a 70 Kg person, or 160 times less than the lethal dose. The product has been approved by the Japanese Ministry of Health and the United States Food and Drug Association (FDA) as long as there is a warning label on the package and that all the films and printing inks used conform to regulatory requirements. The U.S. Department of Agriculture (USDA) also approved its use in indirect contact with beef jerky, dehydrated meat and poultry products.

Under **ideal** stoichiometric conditions, one gram of ferrous iron consumes 3.36×10^5 liters of oxygen if the iron were in solution and totally available, making this by far the most effective oxygen scavenger material in commercial use. In the large particulate form, less iron is available, but in the ferrous iron powder form, the powder disintegrates rapidly and so most of the iron becomes available. For an 0.003 inch gauge polyester film with oxygen transmission rate of 4 cc/m²/day, a sachet containing one gram of iron should be able to handle the oxygen permeating in for 84 days for a square meter surface area package. This computation assumes that the oxidation rate to the ferric state is faster than the diffusion rate of oxygen into the pouch. Instead of a sachet, this amount of iron might be spread out over the entire surface area of a film if it were entrapped so as to not enter the food, as has been done by Multiform Desiccants in its FreshMax® label product discussed below.

Assuming hermetic seals, the amount of iron that must be used depends on the initial oxygen level in the headspace, the amount of dissolved oxygen in the food or beverage and the film oxygen permeation rate. Although it is not easy to calculate all of the above factors, the general rule in reality is that one gram of iron actually reacts with 300 cc of oxygen. One Ageless® configuration designed for contained product with water activities of less than 0.85 requires one to four days to reach 100 ppm residual headspace oxygen. In-package oxygen scavenger sachets are available in sizes that can react with 20 to 2,000 cc of oxygen based on using packages with oxygen permeabilities no greater than 20 cc/m²/day.

Other Ageless® types function better at higher water activities and have faster reaction rates (zero to two days) with the same oxygen scavenging capacity. One type does not absorb oxygen until exposed to water activity greater than 0.85, and so can be handled if kept dry. Other types require that they be handled in a low or zero oxygen atmosphere since they begin to react immediately.

Various suppliers have demonstrated significant shelf life improvement with the oxygen scavenging sachet. For example, white bread shows mold growth at ambient

temperature in air in four to five days while with the sachet in the package, mold-free shelf life can be more than 45 days. Pizza crust which molds in two to three days in air at 86°F will be mold-free for more than ten days. Removal of oxygen also eliminates beetles in stored flour packages which may be a significant problem in humid environments. Ageless® sachets are claimed to be able to keep packages of snack foods at less than 0.1% oxygen over a period of three months at ambient temperature.

It must be pointed out, however, that an oxygen-free atmosphere in foods with greater than 0.92 water activity can be conducive to the growth of pathogenic anaerobic microorganisms such as Clostridium botulinum. Thus, use of the sachet under certain conditions could be dangerous if the temperature is not kept at 3°C or below. Several researchers have demonstrated that unprocessed fish packages containing sachets showed rapid development of botulism toxin in fish without necessarily exhibiting signs of spoilage.

Another problem is that the iron-containing sachet can trigger on-line metal detectors, which is one rationale for using ascorbic acid in-package oxygen scavenger sachets.

As indicated above, most of the developments on the application of ferrous compounds as oxygen scavengers stem from Japan's Mitsubishi Gas Chemical Company.

A. American Organizations

i. Multiform Desiccants, Inc.

Almost all of the United States' development on iron-based oxygen scavengers has been from Multiform Desiccants. Most of Multiform Desiccants' early program was with sachets, and more recently with flat attachable adhesive-backed labels or patches which they have trade named "FreshMax®."

This company, which is the United States' leader in production in this field, has been manufacturing oxygen scavenger sachets since 1988 and has made 14 million through mid-1994. Their scavengers have capacities from 20 to 2,000 cc of oxygen and are all ferrous based. Among their commercial applications are bakery goods, processed meats, nuts, real bacon bits, chilled pasta, pizza crusts, and military rations (e.g., MRE bread, cake and snack items and Tray Ration hamburger buns).

Multiform Desiccants regards the patches as interim steps towards incorporating oxygen scavenging materials directly into package wall materials. Evidently they have some means of incorporating the materials into semi-rigid pharmaceutical packages but not into flexible packages. During Pack Expo '94, the company announced that they

are applying for a patent on an oxygen absorbent package structure currently under development in their laboratories.

Among their developments in progress are incorporation of the scavengers into package materials and retortable oxygen absorbers. Meanwhile, the flat or label versions (using Japanese Asahi applicating equipment and double-sided tape) are adhered to the package materials in commercial meat packages marketed by the U.K.'s Marks & Spencer retailing organization.

Multiform Desiccants' patents on which their commercial products are based begin only in 1991. The first cited (Cullen et al., 1991) is a combination of ferrous iron plus 10-14% sodium chloride plus silica, i.e., silicon dioxide, and DuPont Tyvek® spun-bonded highly gas permeable polypropylene sachet material. The reasoning is that during formulation and handling, the scavenger is dry and therefore inactive. The electrolyte or salt, representing 10-20% of the total, is carried on the silica. The water-attracting material represents about 8-14% by weight of the blend and the iron compound, 20-40% of the blend.

The water-attracting component has greater affinity for the electrolyte than does the oxygen-attracting component, and so the electrolyte will not combine with the iron. When exposed to an environment in which the relative humidity is in the 90% range, the moisture activates the electrolyte so that the oxygen is scavenged by the iron. In their patent example of a packaged quiche, oxygen concentration was reduced from the 20.9% of air to 0.15% within 36 hours.

A later Multiform Desiccants' patent (Cullen et al., 1992) described the same oxygen scavenging system for liquid contents but not in a sachet. Rather, the dry components were in a cylindrical cartridge that floats on the liquid within a can or jar and removes oxygen from the headspace.

In 1993, Multiform Desiccants was granted a patent on an oxygen absorber capable of removing oxygen from a low moisture product. In this development, the iron and the electrolyte were complemented by a hydrogel that provides water for activation. As with other sachets, the packet was fabricated from spun-bonded polyolefin, i.e., polyethylene, that readily transmits gas. The hydrogel is an amorphous silicon dioxide which can contain up to 70% moisture and remain as a flowable powder. The hydrogel was reported to provide enough water to produce an electrolytic solution to cause a rapid reaction of the iron with oxygen. Products with moisture contents as low as those of potato chips were indicated as examples of packaged products in which virtually 100% oxygen absorption is accomplished within 36 hours.

The system described might be of interest for packaging of dry products, but, of course, the hydrogel would eventually surrender all its water, after which the oxygen

scavenging action would cease.

An interesting variation on the basic iron system was disclosed in another Multiform Desiccants' patent (McKedy, 1993). The iron was particulate size annealed electrolytically reduced iron 100 to 325 mesh. According to the developers, such forms of particulate iron as hydrogen reduced iron, atomized iron and milled or pulverized iron absorb oxygen relatively slowly. Electrolytically reduced iron absorbs oxygen at a faster rate and an-nealed electrolytically reduced iron absorbs at an even faster rate, especially at temperatures below 10°C. Annealing is reported to change the structure of the electrolytically reduced iron by increasing the surface area, which in turn causes the iron to be more active in oxygen absorbing capacity.

Data presented indicate that conventionally reduced iron particles absorb 29 cc of oxygen in seven hours, and annealed electrolytically reduced iron absorbs 100 cc in six hours, or about a four times faster rate. The materials with electrolytes present to effect the reaction were inserted in gas permeable sachets for insertion into closed packages.

Although Multiform Desiccants is not a large company with vast research and development facilities, it is probably the best resourced and best equipped American commercial enterprise to lead development in the application of oxygen scavengers into package materials. Such development would probably have to be conducted in cooperation with a package material converter. It is our understanding that at the time of preparation of this report, they are without a Director of Research and Development. Nevertheless, they have developed a package material incorporating an oxygen scavenger which they expect to commercially introduce in 1995.

ii. United Desiccants

A producer of in-package desiccants (e.g., activated clay, silica gel and molecular sieve moisture absorbers), United Desiccants has represented at least one Japanese ferrous oxygen scavenger manufacturer during the past ten years. Currently, they do not have oxygen scavengers in their product mix but intend to begin making them in 1995.

iii. Engelhard

Engelhard Corporation in the United States has been supplying bentonite and montmorillonite clay moisture absorbers under the Dryguard and Desiccate trade names since the 1950s. They do not currently offer oxygen scavengers.

iv. Amoco Chemical

This company has been developing a proprietary oxygen scavenging system that is

incorporated directly into plastic package materials. The nature of this scavenger has not been revealed.

v. Liquid Air

U.S. Patent 4,840,280 to Liquid Air (Schvester, 1990) is specifically directed to the use of ferrous iron to address the question of oxygen in beverage packages such as beer bottles. Oxygen scavenger quantities sufficient to rapidly absorb the volume of oxygen in the headspace of the container after filling and sealing operations is contained within or on the surface of the container's lid or cap, and is adapted to be in contact with the contained liquid. To avoid the direct contact of the chemical with the liquid, a film that is very highly permeable to gaseous oxygen (10,000 cc/m²/atm/hour or greater) and water vapor, but impermeable to liquids, is used as barrier between the scavenger and the contained liquid. Suggested films include rubber (polydiakyl siloxane) or poly-tetra fluoroethylene (PTFE) -based component. The combination of oxygen scavenger and protective film is introduced during the closure manufacture. This closure device can be used in association with an inert gas flushing process to reduce the gas consumption involved in this technique (which should be done with all scavenger systems). Once in place, the oxygen absorption reaction is initiated and the residual oxygen in the container's headspace is removed. The partial pressure of oxygen can be lower than 0.01%. The velocity of oxygen absorption is a function of the film permeability and of the amount of available scavenger in the cap. In an industrial process, these values were chosen to reach an oxygen partial pressure lower than 0.5% after less than thirty minutes. The patent indicates that the scavenger is iron oxide powder applied in a closure which is used with beer. In a cited example, the 14 ml of headspace of in a bottle of beer was flushed with nitrogen down to 3.5% oxygen. The reaction of the scavenger caused a decrease to 0.5% oxygen in one hour and to 0.2% oxygen in two hours.

B. Japanese Organizations

This section discusses a select few of the many Japanese companies offering oxygen scavengers, emphasizing those that are currently offering their products in the United States.

i. Mitsubishi Gas Chemical

As cannot be over emphasized, Mitsubishi is the world and United States' leader in oxygen scavenging technology and sales, especially for iron based absorbers, although they also have ascorbic acid-based and other absorber products. They have been producing and marketing oxygen scavengers since 1977 and claim to have produced approximately eight billion since their introduction. All of their Ageless® oxygen scavengers are manufactured in Japan, and they have been marketed in the United

States since 1984. Cryovac Division of W.R. Grace & Co. has been their United States distributor since 1990. Among the American end users of Mitsubishi oxygen scavengers are Kraft General Foods for DiGiorno fresh pasta, and Curtice-Burns, Goodmark, Hormel and Dorskocil for cured meats.

Mitsubishi Gas Chemical's iron technology is basically reduced iron powder plus sodium chloride and zeolite in a gas permeable sachet for placement in a hermetically sealed gas barrier package. Their label application technology, which has been reported by them, has not yet been commercialized.

As early as 1979 (Komatsu et al., 1979), Mitsubishi Gas Chemical was granted a United States patent on sachets containing iron sulfite as the oxygen scavenger. The constituents of the oxygen absorber include iron salt; 0.1% sulfur, to prevent evolution of hydrogen gas; 0.01 to 5 parts of a metal halide or sodium sulfate, sodium sulfite or sodium bicarbonate; binders such as sodium alginate, carboxymethyl cellulose and starch; and a polyvalent alcohol such as ethylene glycol. These materials were blended into a granular form and placed in perforated and gas permeable polyethylene or cotton fabric pouches for placement inside hermetically sealed packages.

When exposed to moisture, the iron compound reacted with oxygen, with one gram of iron powder being capable of removing 30 to 70 cc of oxygen after 20 hours, and 125 to 135 cc after 160 hours within a one liter package.

U.S. Patent 4,299,719 to Mitsubishi Chemical Co. discloses a method in which ferrous carbonate is the oxidizable material. One mole of carbon dioxide is produced for each mole of oxygen reacted. An aqueous reaction medium and 0.01 to 5 parts of iron per part of ferrous carbonate are required. The patent also requires a metal halide, preferably NaCl, as a catalyst. In the presence of fresh foods of high a_w , no water is needed since the system absorbs the moisture from the internal environment. A metal hydroxide is also incorporated to elevate the pH so that the carbon dioxide will evolve into the gas phase thereby to replacing the volume of oxygen reacted.

Iron-based oxygen absorbers were applied into bottle closures in a 1981 Mitsubishi Gas Chemical Co. patent (Moriya, 1981). In this application, a gas permeable film pouch containing the oxygen absorbents was placed in the liner of the bottle closure and separated from the liquid contents by a gas permeable membrane. The film prevented the oxygen absorbent from direct contact with the package contents. Oxygen absorbents listed were iron powder, oxalates, sulfites, dithionites, pyrogallol, zinc powder and glucose.

In 1983, Mitsubishi Gas Chemical was granted a patent in which the oxygen absorber in the gas permeable pouch (sachet) was specifically applied to extend the shelf life of processed fish and roe packaged in gas impermeable bags. Among the

oxygen absorbents mentioned in addition to iron were iron carbide, hydroquinone, BHA, ascorbic acid and erythorbic acid.

Two 1984 Mitsubishi Gas Chemical patents (Ohtsuka et al., 1984) detailed the construction of the gas permeable sachets to contain the oxygen absorber. Specifically cited were the gas permeabilities required for passage of air. Among the materials suggested were spun-bonded polyolefins such as DuPont's Tyvek® spun bonded polyolefin and microporous polypropylene such as Celanese Celguard®. Bonding agents included ethylene vinyl acetate and ionomer extrudable adhesives.

These concepts are further refined in a 1986 patent (Ohtsuka, 1986) in which the objective is to employ plastic materials that do not absorb moisture and to avoid distortion of the perforations which might permit some of the granular oxygen scavenger particles to leak through the wall.

In 1987, Mitsubishi Gas Chemical received a patent for a cup-shaped "packet" which is effectively moisture-impermeable (Wakamatsu, 1987). In this development, the oxygen absorbent packet contains the moisture required for actuation. The cup is closed with a gas permeable membrane which is heat or adhesive sealed to the flange. This development is evidently intended to be a packet to be inserted into a jar of, for example, vitamin C tablets.

Another bottle closure oxygen scavenging device was described in 1988 (Morita et al., 1988). Again, a sachet containing the scavenging material is placed in a compartment in the liner of the closure separated from the liquid contents by a membrane. This development is characterized by the presence of a vacant compartment above or behind the scavenger sachet-containing compartment to assist in ensuring the hermetic seal of the closure.

An important 1988 (Inoue, 1988) patent from Mitsubishi Gas Chemical describes a label sheet containing the oxygen scavenger. In simple form, the label is a mixture of fibrous material, iron powder, water and an electrolyte formed by a process similar to paper making. The developers recognized shortcomings that were, and continue to be, deterrents to commercial applications of oxygen scavengers:

1. There is the risk that the consumer may accidentally consume the oxygen scavenging agent.
2. Since the sachet cannot be made into an extremely small size, it is not applicable to a package having a very small inner space.
3. If a food container has a narrow opening, the oxygen scavenger cannot be inserted into the container.

4. When an oxygen scavenger is to be fixed within a tray having a certain thickness, the oxygen scavenger causes an increase in the height of the tray, presenting difficulties in manufacturing the tray and also in securely fixing the oxygen scavenger in place.
5. The oxygen scavenging powder filled in a bag tends to coagulate into a lumpy shape and has a reduced surface area contacting air. Therefore, to produce the scavenging of oxygen at a desired rate, it is necessary to provide a larger quantity of oxygen scavenging powder than with the theoretical oxygen-scavenging capacity.

The 1988 development was intended to provide a sheet-like oxygen scavenger which can be securely fixed to the inner wall of a package.

Fibrous material is used as a carrier of iron powder, water and electrolytic material and is intended to increase the contact area between iron and air. The fibrous material is prepared from natural or synthetic fiber and may be pulp, acrylic, nylon fiber, viscose rayon fiber, polyethylene or polypropylene fiber, with the preference being pulp and/or polyethylene fiber.

To achieve a thorough mixture of iron powder with fibrous material, the iron should have a particle size less than 0.25 mm or preferably 0.15 mm. The electrolytic materials needed to accelerate the action of the iron powder compounds include NaCl or CaCl_2 , and are dissolved in water.

It is possible to add sizing agents normally applied in the paper making process, such as coloring materials, paper-reinforcing agents, water-repellents, and oil-repellents to enhance the sheet. The gas permeability of the sheet-like oxygen scavenger selected is less than 5,000 seconds/air/100 ml in Gurley type air permeability measuring devices.

Preparation in sheet form is accomplished by suspending the fiber, iron powder, water and electrolytic material, and then filtering the suspended solid to dehydrate it to a water content of less than 40% by weight, thereby forming a sheet-like material. The concentration of solids in the suspension is controlled to a range of up to 9%. The concentration of the fibrous material in the suspension is from 0.1 to 3% by weight based on the total weight. The content of the iron powder should be controlled to range from 0.1 to 3% by weight based on the total of the fibrous material, iron powder, water and electrolytic material. The fibrous material is suspended by means of a pulper in an aqueous solution of the electrolyte. The suspension is introduced into a paper machine and screened through wire cloth. The fibrous material that has been filtered out is then suctioned, dehydrated by pressure, and thermally dried. In the sheet form, the iron powder accounts for 10 to 1,000 parts by weight, the electrolytic material ranges

between 0.002 and 100 parts by weight and the water content ranges from 1 to 400 parts by weight. The sheet thickness ranges between 0.1 and 5 mm. The sheet can be sealed in a package having a good gas barrier property together with, for example, foods or other articles. When coated with or wrapped in a film, the sheet can be isolated from package contents to avoid contamination.

The surface of the sheet may be covered with an oxygen permeable plastic such as PVC or silicone by dipping, casting or by laminating to a microporous film. From the standpoint of waterproofness, spun-bonded non-woven microporous polyethylene sheet such as Tyvek® is the preferred material. "Microporous" film is a plastic film having a multiplicity of very fine openings and a Gurley air permeability of 0.01 to 10,000 seconds/air/100 ml, which under atmospheric pressure, does not permit water to pass.

When both sides of the non-woven fabric or microporous film are laminated with plastic film, the film covering the outside of the non-woven fabric or microporous film should be formed from a gas barrier lamination such as polyester/polyethylene, nylon/polyethylene or oriented polypropylene/polyethylene. The thickness of the wrapper need not be restricted but generally is less than 5 mm. The preferred wrapper includes paper, non-woven fabric, microporous film and sheet laminated on one or both surfaces of the paper, non-woven fabric or microporous film with a plastic film containing many small pores or a reinforcing sheet.

As indicated above, Mitsubishi Gas Chemical has not yet commercialized this sheet as a package material.

A 1989 Mitsubishi Gas Chemical patent (Inoue, 1989) describes a sachet for oxygen scavengers that is specifically intended for use within retort pouches. The differentiating variable is the impregnation of the sachet material with a fluorine resin in the form of an emulsion. The fluorine resin coats the entire fiber to provide air, water and fat resistance. The fluorine resins cited are various tetrafluorides and hexafluorides such as ethylene tetrafluoride.

ii. Toyo Seikan

Regarded as the largest package supply company in the world, Toyo Seikan's marketing has been largely confined to the Far East. A 1993 patent issued to Toyo Seikan describes a film lamination, i.e., a package material containing a ferrous oxygen scavenger. Although the emphasis is on the incorporation of the oxygen scavenger into a bottle closure liner, a clearly described alternative is a package film.

In conventional practice, since the resin has a high oxygen permeability, the oxygen-absorbing speed is much lower than the oxygen-absorbing speed attained when a paper packaged oxygen-absorbing agent is directly charged, and the oxygen-

absorbing effect is not satisfactory.

The primary objective of the development is to provide a heat-formable oxygen absorbing resin. The development consists of an oxygen absorbing resin, composed of a heat-formable resin having an oxygen permeation coefficient higher than 10^{-12} cc/cm² seconds at a temperature of 20°C and 0% RH, and an oxygen scavenger. The resin used is a blend of a polyolefin with a water-absorbing resin (such as a modified polyethylene oxide), a vinyl alcohol polymer, a sodium acrylate polymer and an acrylic acid/vinyl alcohol copolymer with an olefin resin.

Water-absorbing resins are ordinarily inferior in heat formability. Each water-absorbing resin mentioned as a blend component in the invention has relatively good extrudability, heat resistance and formability. However, if the resin is used solely in the presence of an oxygen absorbing agent, its deterioration is promoted by the effect of the oxygen absorbing agent. This problem is overcome by blending an olefin resin with the water-absorbing resin to produce excellent heat stability and formability. Thus, the method can be used to produce a resin composition suitable to fabricate a lamination. The composition can be used for absorbing oxygen in multilayer package structures.

It is important that the oxygen absorbing resin has each of the following three characteristics: the oxygen permeation coefficient at 20°C and 0% RH is greater than 10^{-12} cc/cm² seconds; water absorption in pure water at 20°C is at least 1%; and the composition is heat formable.

To include an oxygen scavenger into the packaging material, it is necessary to disperse the oxygen scavenger into the resin. The resin has water-absorbing properties, and since this water-absorbing resin is always present around the oxygen scavenger, water is effectively utilized for the oxidation reaction. Resins with high water absorption generally are not easily formed with heat. Thus, if the resin is melt-kneaded with an oxygen scavenger, discolorations from molecular dehydration and consequent cutting of the main chain or crosslinking can occur. These problems can be solved by using blends of polyethylene oxide, vinyl alcohol polymer, sodium acrylate polymer or acrylic acid/vinyl alcohol copolymer with an olefin resin.

All of the oxygen scavengers customarily used were suggested for use singly or in mixtures of two or more. Further, these oxygen scavengers can be used in combination with accelerators, such as hydroxide, carbonates, sulfites, halides of alkali metals and alkaline earth metals.

The particle size (median diameter) of reducing iron ranged from 0.1 to 100 μ m. When the particle size is smaller, the oxygen absorbing capability is greater. However, if the particle size is smaller than 1.0 μ m, when mixing or kneading in air to blend, heat is generated, and so mixing in nitrogen becomes necessary.

As the oxidation promoter, an electrolyte free of a copper or a sulfur component is used. A chloride of an alkali metal and/or alkaline earth metal such as NaCl plus CaCl_2 is preferred. If this oxidation promoter is used in combination with a manganese salt such as manganese chloride (MnCl_2), the absorption of oxygen is effectively enhanced.

The reducing iron and oxidation promoter is used in a weight ratio ranging from 98%/2% to 90%/10%. The oxidation promoter could be 0.05 to 15.0% by weight of sodium chloride, 0.01 to 15.0% by weight of calcium chloride and 0.01 to 5.0% by weight of manganese chloride. Carriers such as active carbon and active alumina are used.

The modified polyethylene oxide used as the water absorbing resin includes polymers obtained by graft modification of polyethylene oxide with an ethylene-type unsaturated carboxylic acid or the acid anhydride such as maleic anhydride, acrylic acid and methacrylic acid. The resin has high water absorption because of multiple repeating ether units and graft-modified carboxyl groups. In addition, the ether groups lead to excellent heat resistance and good heat formability. The proposed vinyl alcohol polymer is ordinarily used for producing films. The polyolefin resins to be blended with the water absorption resin include, for example, low-, medium- or high-density polyethylene, polypropylene, ethylene-propylene copolymers, EVA and ionomers, in a ratio of 10% polyolefin to 90% water absorbing resin.

The oxygen scavenger is incorporated in an amount of 5 to 200 parts by weight, per 100 parts by weight of the resin. If the amount of the oxygen scavenger is below this range, the oxygen absorbing performance tends to decrease, and if the quantity of the oxygen scavenger exceeds this range, heat formability is often degraded.

The oxygen absorbing resin composition can be applied to the inner surface of a package so that the layer of the resin composition is exposed, or the oxygen absorbing resin composition can be arranged on the inner surface side through a thin layer of a moisture resistant resin such as an olefin resin. In the latter case, the moisture resistant resin layer prevents direct contact between the oxygen scavenger and the package contents. A layer of microporous material or a layer with a large number of perforated micropores may be used to permit oxygen to pass freely through the thin layer. A one to 20 μm layer allows permeation of oxygen and water vapor, and prevents direct contact between water and the oxygen scavenger. The inner layer permits heat sealing and acts as a protective layer. It is believed that Toyo Seikan has marketed this structure in Japan as an oxygen scavenging sheet.

Toyo Seikan was issued a patent on a multilayer retortable plastic can that incorporated an oxygen scavenger into a moisture-absorbing layer (Koyama, 1992). The basic oxygen barrier cited in the patent is ethylene vinyl alcohol (EVOH), a plastic with well-known water sensitivity. Among the mechanics to obviate the loss of oxygen

barrier as a result of water have been to place a desiccant or water absorber adjacent to the ethylene vinyl alcohol. This patent is not unlike the American Can developments using sulfites. In this manner, water that penetrates the plastic at higher rates during retorting is absorbed before reaching the ethylene vinyl alcohol.

In this Toyo Seikan development, the oxygen scavenger is incorporated into the gas barrier, i.e., EVOH, which functions as a moisture absorber particularly under retort conditions; the EVOH thus triggers the oxygen scavenger to remove oxygen. This concept is intriguing since the ethylene vinyl alcohol is a mediocre oxygen barrier when wet, and the oxygen scavenger only functions when wet. Thus, the oxygen scavenger, wet from the retorting process, compensates for the ineffectiveness of the EVOH during these circumstances. Evidently, the action of the oxygen scavenger must be triggered by the presence of a water absorbing material such as sodium or calcium chloride.

The oxygen scavenger is essentially an iron compound. The developers identify an alternative oxygen scavenger as a high molecular weight compound with a polyhydric phenol, such as polyhydric phenol/aldehyde resin, in the skeleton.

The oxygen scavenger is incorporated into the moisture absorbing oxygen barrier resin layer sandwiched between the moisture-resistant inner and outer layers. The methods described for incorporation include melting EVOH copolymer resin and mixing it with the powdered iron particles at a ratio of 7% scavenger by weight. Mixing is performed in a high speed stirring vane-type Henschel mixer. This mixture is then extruded into pellets used later for coextrusion into the multilayer sheets, one layer being the EVOH/iron mixture. Since the layer of EVOH/iron is sandwiched between opaque polypropylene layers, no issue of color or of opacity of the layer is raised.

Results of testing of oxygen concentrations within trays thermoformed from the coextruded sheet indicate that the presence of the oxygen scavenger can reduce the headspace oxygen by factors of five to ten.

The concept of this structure (marketed under the trade name Oxyguard™) is described by Toyo Seikan and appears to have merit as a means to provide an all-plastic structure in either flexible or semi-rigid form. Oxyguard™ could function as a significantly better oxygen barrier than a conventional material and, additionally, continuously remove oxygen from the package headspace. The technology has been reduced to developmental commercial practice in packages of aseptically package wet rice that is very popular in Japan. These packages consist of thermoformed coextruded multilayered PP/EVOH/PP trays, conventionally with oxygen scavenging sachets inserted. In Toyo Seikan's version, used to package Sato Foods' rice, the scavenger is incorporated in the layer between the PP and the EVOH. Toyo Seikan claims the absorbent package cost to be the same as the conventional package cost.

This package marks the first commercial application of oxygen absorbent materials built into an actual food package structure.

iii. Sumitomo Chemical

Not a known leader in oxygen scavenging technology in Japan, Sumitomo Chemical nevertheless is a significant Japanese packaging technology innovator.

A 1992 patent assigned to Sumitomo Chemical (Na Kae et al., 1992) describes an oxygen absorbing plastic sheet characterized by small microvoids formed by stretching the plastic containing the oxygen absorber. Because the uniformly dispersed oxygen absorbent is in contact with air contained in and entering the microvoids, the stretched sheet effectively absorbs oxygen in the air. The oxygen absorbent is iron in the form of carbides or oxides, with a particle size of 1 to 50 μ m. Suggested electrolytes include sodium, calcium or magnesium chloride adhered or coated onto the iron powder surface, or alternatively, blended with the powder at a rate of 0.1 to 5% by weight.

The sheet as reported does not absorb any significant amount of oxygen at low relative humidity, but is activated when the relative humidity exceeds 50%. The oxygen absorbent constitutes more than 30% by weight of the total sheet, with concentration of 30% of the total leading to a reduction in the number of microvoids.

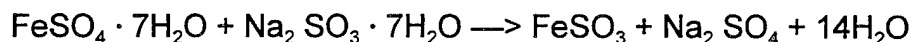
Thermoplastics cited by the company include various polyethylenes with at least 10% very low density polyethylene (density 0.87 to 0.91 grams/cc). Gauge of the unstretched sheet is up to 5 mm. In the process, the oxygen absorber is mixed with the thermoplastic in a Banbury mixer at a temperature of up to 84°C and extruded through a T-shaped die to obtain a one mm gauge sheet. The sheet is stretched 3.2 times at 60°C in the machine direction. At a stretch ratio of less than 1.5, microvoid formation is reportedly insufficient, while at a stretch ratio above 8, the film is too weak. The resulting film is capable of oxygen absorption at a 12 cc per hour rate, at elevated relative humidity.

This development is interesting in that monoaxial orientation produces microvoids where, according to the developers, the majority of the oxygen reaction occurs. Although dependent on the plastic to have a high oxygen permeability, the microvoid concept certainly increases the exposed surface area very significantly.

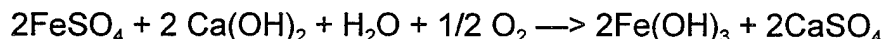
iv. Toppan Printing

Japan's second most important producer and marketer of oxygen scavengers generally has emphasized ascorbic acid scavengers probably to differentiate itself from the leader, Mitsubishi Gas Chemical. In a 1983 patent, Toppan described a system in which they combine iron with ascorbic acid to produce the oxygen scavenging effect

with the advantage that no moisture was required. The mix proposed includes iron, ascorbic acid, an alkali compound, a sulfite and a sulfate. Water is generated by the reaction of the sulfite and the sulfate (or chloride). In a typical reaction:



The water supplied from the product and the alkali compound reacts with each other to absorb oxygen:



These reactions are employed in concert with iron powder and ascorbic acid to remove oxygen.

Toppan's means of exposing the package contents to the oxygen scavenger is to use a sachet of paper plus porous or perforated polyethylene film within the sealed package.

C. European Organizations

i. PLM

In Europe, the noted Scandinavian package material converter PLM developed an oxygen scavenging system in which metal ions, presumably iron, are mixed in a plastic melt to be coextruded in film or sheet form (Anon., 1990). As in so many other systems, the permeation of the oxygen through the plastic leads to a reaction. According to PLM, the system was also produced in a lacquer form to coat the interior of containers.

ii. Atco SA

In Caen, France, Atco SA launched a range of oxygen absorbers in 1989 (Askenazi, 1989). Under the trade name Atco, these are evidently iron powder in gas permeable sachets to be placed in cheese packages.

12. Economics

Questions exist concerning the economics of introducing iron powder into independent sachets or component compartments. Cost appears to be an obstacle to the commercial acceptance of in-package scavenger sachets. A sachet capable of removing 25 to 30 cc O₂ would cost about \$0.02 to \$0.03. To reduce O₂ to 0.3% without mechanical vacuum would require up to \$0.10 to \$0.30 of oxygen scavenging sachets. Although one gram of iron can theoretically remove 200 cc of O₂, the

efficiency is about half that due to particle agglomeration.

With the wide experience of using iron as an oxygen scavenger, it should be expected that in all applications in which oxygen is a problem, this will be the first material proposed and tested.

13. Developmental

One of the more intriguing of the oxygen scavenger products for package materials emerged in 1991 from United States' chewing gum manufacturer Wm. Wrigley, Jr. The objective of the Wrigley development reported in patent form (Courtwright et al., 1991 and 1992) is to provide a long term flavor delivery system through emission from materials in the package structure. During the course of this development, the researchers postulated that the reverse reaction, oxygen scavenging, could be performed by the same technology. This action could help to preserve the flavor of the contained chewing gum. The proposed technology suggests incorporating the oxygen scavenger into porous plastic beads which, in turn, is imbedded as a coating in the primary package material immediately adjacent to the product. Although they suggested that iron be employed as the scavenger, virtually any oxygen scavenger could be used. Among the other oxygen absorbers suggested were BHA, BHT and glucose oxidase. In the actual laboratory work, the researchers used Mitsubishi Gas Chemical's Ageless® iron oxide/activated charcoal as the oxygen scavenger. The relatively little laboratory experimentation conducted was largely to demonstrate the ability to incorporate the scavenger into the package structure. No data were reported on the oxygen scavenging capacity of the structures.

The Wrigley development involves mixing the iron/activated charcoal with edible oil and soaking the porous beads with the mixture. The loaded microbeads are then blended with a mixture of microcrystalline and paraffin waxes which were then used as the laminant in a PVDC (exterior)/polyethylene lamination. Oxygen from within the package passes through the polyethylene into the oxygen scavenger layer. An alternative package structure is the classical chewing gum wrap of aluminum foil/wax/strike-through tissue in which the wax contains the loaded microbeads, and through which gas can pass through the wax into the microbeads and their active component. Among the problems encountered in the brief experimental period was the occurrence of residual plastic monomer, which led to off-odors. Wrigley has abandoned the project but would be interested in divesting of its interests in its patents.

The Wrigley research is based on porous plastic beads developed by Advanced Polymer Systems of Redwood City, California, capable of adsorbing and desorbing gaseous compounds. This start-up research and development company's trade name for their product is Microsponge. In a joint venture with Dow Corning, the product is

marketed by the larger partner under the trade name of Polytrap.

Advanced Polymer Sciences manufactures the adsorbent porous beads, which are less than 40 microns in diameter. The beads are made mostly from acrylates, or from styrene divinyl benzene for the Wrigley work. The adsorption process is proprietary, but may require solubilization of the component in a solvent such as water. No reconciliation of this stated requirement with iron powder was offered. Up to 50% by weight iron loading is reportedly possible. The particles may be loaded, adsorbed, desorbed and reloaded repeatedly, according to the California group. Advanced Polymer Sciences expressed a desire to work with U.S. Army Natick R,D&E Center on further developing the concept.

A. Ascorbic Acid-Based Absorbers

Second in commercial importance to iron compounds as oxygen scavengers are ascorbic acid and its derivatives. Ascorbic acid, which is vitamin C, is sometimes employed as a food or beverage ingredient, "oxygen interceptor" or antioxidant, as well as a nutrient.

Because ascorbic acid is a six carbon compound, the weight required to react with oxygen is quite high. Like iron, it is readily but not quickly oxidized to dehydroascorbic acid, which is relatively innocuous. (Some argue that the reaction is not oxidation but rather hydrogen transfer, which would reduce its stoichiometric oxygen reaction capacity; regardless, ascorbic acid reacts with and removes atmospheric oxygen). The conversion to dehydroascorbic acid is catalyzed by the presence of metal ions such as iron.

Ascorbic acid is an expensive chemical to employ as an oxygen scavenger, because it is not synthesized commercially: it is derived either by extraction from natural plant material of which it is a small constituent, or by other biological means.

Ascorbic acid is used as an intentional oxygen scavenger by Toppan Printing in its "C" type products. According to Toppan, for unspecified reasons iron compound scavengers do not function in the presence of carbon dioxide. On the other hand, ascorbic acid functions well in the presence of carbon dioxide. Hence, Toppan employs their "C" or ascorbic acid-type for applications in the presence of carbon dioxide such as in packages of roasted and ground coffee and bread. Among the other attributes of ascorbic acid as an oxygen scavenger is its non-response to metal detectors on packaging lines. Without further explanation, Mitsubishi Gas Chemical employs the ferrous iron scavenger in the high CO₂ environment of roasted and ground coffee.

Grace Daraform's oxygen scavengers incorporated into plastic bottle closure linings

(discussed on page 76) are ascorbic acid analogues. Since these are intended to some degree to be used in the presence of carbon dioxide in beer and soft drinks, the claimed carbon dioxide reaction with iron might be a reason.

Ascorbic acid functions only in the presence of water. Therefore to function as an oxygen scavenger, it must either be accompanied by water or else water must be supplied from the environment.

Because of its oxygen sensitivity, ascorbic acid must be very difficult to incorporate into a plastic compound such as suggested for the Grace Daraform liner materials. An anaerobic environment is probably required.

Despite its known ability to react with oxygen, ascorbic acid is expensive for the quantity of oxygen removed and somewhat difficult to use. Japan's Toppan Printing admittedly employs ascorbic acid as their chief oxygen scavenger to differentiate themselves from Mitsubishi Gas Chemical's ferrous Ageless® product. Toppan has a range of iron-based scavengers but sells relatively few, probably because of the difficult competitive situation in Japan.

i. Pillsbury

Dr. Ernst Graf (1994) was granted two patents assigned to the Pillsbury Company covering the use of ascorbic acid analogues whose action could be accelerated by the presence of copper, a well-known reaction generally avoided in most food situations. Dr. Graf recognized that the copper is highly reactive in food. The developer indicated that the oxygen removal with copper plus ascorbic acid is so rapid, i.e., 2-3 minutes, that no oxygen could be detected in a closed package. This development is not for packaging, but rather for incorporation of the scavenger directly into the food. Were it not for the copper component, this might be an interesting route to examine.

This development was used by Pillsbury for several refrigerated Mexican food sauces marketed during the late 1980s. Currently, the food application rights are owned by Pillsbury and the non-food applications belong to the inventor. Now with another organization, Dr. Graf indicated his desire to work with U.S. Army Natick R,D&E Center to apply the system to package materials.

ii. W.R. Grace & Company

As indicated above, W.R. Grace has been one of the two United States' companies directly involved in development of oxygen scavenging package materials as well as acting as a sales agency for Mitsubishi Gas Chemical's Ageless® products. A large worldwide company, Grace has not concentrated its oxygen scavenging activities in a single location. Its bottle closure gasket developments are in the United Kingdom. As

indicated previously, all employ ascorbic acid or analogues as the core oxygen absorber.

Grace's oxygen absorbent bottle gasket liners have been marketed in both the United States and Europe since about 1990. The original patent (Hofeldt et al., 1992) describes a sealing compound formed from a composition that can be extruded into a bottle closure to become a gasket. The developers noted that the compound can be either a bottle liner or a liner in a double seamed can end. The material, essentially ascorbic acid in a plastisol compound, can resist thermal pasteurization.

The oxygen scavengers suggested are ascorbates or isoascorbates plus sulfites, such as sodium sulfite, at a level of 4% to 5%. The plastic materials suggested were either polyethylene thermoplastics or polyvinyl chloride plastisols.

In their next patent directed to beer packages (Hofeldt et al., April 1993), the developers indicate that the same oxygen absorbers in the same polymeric matrix are activated by thermal pasteurization or sterilization. Although the relative humidity in the headspace of a beverage-containing bottle or can is generally sufficiently high to activate the scavenger, the reaction could be accelerated by heating to increase moisture permeation into the scavenger mix. Thus, they suggest a scavenger that remains effectively inert until the pasteurization or sterilization mode. Moisture generated from the interior contents permeates into and becomes trapped within the gasket to accelerate the oxygen removal reaction. Oxygen that is trapped in the headspace, and oxygen that is permeating into the bottle through the gasket, are both reacted with the scavenger.

Typical formulations incorporate the ascorbic acid analogues at only the 2 part by weight level, with sodium sulfate at 5 parts by weight. Ethylene vinyl acetate and polyvinyl chloride are the carriers into polyethylene.

B. Japanese Organizations/Companies

At least three other Japanese patents are among the literature describing ascorbic acid analogues for oxygen scavenging. Two describe pouches containing ascorbic acid, alkaline compounds, an aluminum salt, a reaction accelerator and silica gel (Ueno et al., 1992 and 1993). The objective is to increase the flowability of the oxygen absorbent powder in order to increase the speed of filling the pouches.

A more interesting patent is from Japan's Toray, a significant manufacturer of plastic films, with one oriented PP film plant in the United States (Yamada et al., 1992). This patent described the construction of a laminated flexible material label with an oxygen permeable membrane containing an ascorbic acid oxygen scavenger. An oxygen-permeable film covers the oxygen absorber, which includes an asymmetric

porous membrane whose outer surface is formed as a dense skin layer. Since the dense layer is very thin but porous, oxygen transmission to the oxygen absorber through the oxygen permeable film is high. The oxygen scavenging chemical, possibly ascorbic acid, is within a non-woven material trapped between the porous layer and a high barrier backing.

The asymmetric porous membranes are fabricated from aromatic polysulfone-based materials by casting and quenching in cold water. The support layer is woven or non-woven fabric. The oxygen permeable non-porous layer prevents the contact with the product, with the suggestion that it be a cross-linked polymer of polyorgano-siloxane or poly/4-methylpentene-1. The oxygen absorbent-containing film is silicone, although polyolefins are indicated as alternatives.

Although intended as a label or as the internal liner for a bottle closure, this technology could be applicable to flexible or even semi-rigid packages, and so this technology perhaps warrants some consideration.

C. Oxbar™

One of the most intriguing systems suggested for packaging of oxygen-sensitive products is Carnaud MetalBox's Oxbar™, which is an integration of gas barrier packaging and oxygen scavenging (Cochran et al., 1991). The British company has discontinued its development, but technical work is reportedly continuing with an unidentified American company. Oxbar™ is a chemical barrier system developed specifically to exclude oxygen, possessing the following attributes:

1. Oxygen-specific, i.e., no removal of other components
2. Polymer based
3. A total oxygen barrier
4. Independent of temperature and humidity
5. A long, but finite, lifetime

Developmental focus has been on the polyester (PET)/nylon MXD6/cobalt system because of the extensive research on this combination. The reactive components are the MXD6 nylon (polymetaxylene diamine-hexanoic acid from Toyobo/Mitsubishi, also trade named Nyref from Solvay in Europe) and a cobalt salt. Cobalt catalyzes the reaction of MXD6 with the oxygen passing through the package wall.

Oxbar™ is a polymeric oxygen scavenging system and is therefore readily formed

into containers using standard thermoplastic converting techniques, such as injection, extrusion and injection blow molding. It has been reported that the materials may also be formed into films.

The low levels of reactive ingredients (MXD6 and cobalt) do not significantly modify the physical or processing characteristics of the structural polymer, PET in this case, but do cause a gray color. The materials are combined together as a blend to offer a monolithic structure on existing PET bottle converting equipment.

The Oxbar™ system is reported to provide virtually total barrier to oxygen ingress for as long as the reactants are present. For example, in one liter PET-only versus PET/MXD6 (4%)/Co blend bottles, the reference PET-only bottles shows an oxygen transmission value of 3.5 cc/m²/day at 73°F, whereas the equivalent Oxbar™ variable has a transmission value of less than 0.04 cc/m²/day. The very low level of transmission persists for a period approaching two years under these conditions.

An important feature of the Oxbar™ system is its ability to maintain its barrier properties under elevated temperature and relative humidity conditions. Many barrier polymers exhibit performance loss under high temperature or high relative humidity conditions.

TABLE 2

OXBAR™: OXYGEN SCAVENGING SYSTEM

<u>General System</u>	<u>Specific System</u>
Structural polymer	PET (95-99%)
Oxidizable component	MXD6 nylon (1-5%)
Metallic catalyst	Cobalt salt (50-200 ppm)

In common with other barrier systems, Oxbar™ relies on chemical activity. Thus its barrier properties persist only for a finite time (note: already reported in the range of two years but possibly longer), which is a function of two primary variables: scavenging capacity and rate of consumption. Scavenging capacity depends on the composition of the blend (MXD6 and Co content) and the container wall thickness. Even after the "zero" transmission period is ended, there is very slow return over several months to the expected blend value. Thus, even for low capacity Oxbar™ blends, there is a significant reduction in cumulative oxygen ingress into the package. The quantities of reactive components may be tailored to the composition to provide an appropriate shelf life for particular end uses.

The rate of consumption is a function of factors such as temperature, wall thickness and the particular matrix polymer used. Filled containers demonstrate twice the rate of consumption of empty containers because the scavenging capacity is consumed from both sides of the wall.

Carnaud MetalBox reported on tests conducted with bottles containing various oxygen-sensitive beverages including beer, orange juice and wine. Shelf lives of over six months were demonstrated. In these bottles, enough oxygen scavenging capacity is present to consume more than one year's oxygen entering through polyester bottles. Essentially no oxygen passed into the package in one year.

By itself, nylon MXD6 has FDA approval in the United States for use as a blend with PET at levels of up to 30%. The temperature of use should not exceed 49°C and the alcohol content of the product should not exceed 8%. These conditions cover a range of uses such as cold-filled beer and carbonated beverages.

At their commercial introduction, although permitted by FDA, cobalt salts of organic acids had not been used as polymer additives. Extractability tests using a range of stimulants and conditions detected no cobalt migration from Oxbar™ containers. Nevertheless, because of the paucity of data on the end products of nylon MXD6 oxidation, the company did not apply to the U.S. FDA for Oxbar™ use for packaging aqueous products.

Although the Carnaud MetalBox patents for Oxbar™ did not limit the application of the nylon MXD6 oxygen scavenger to PET, it stated the PET systems as functional. This system would be useful in any plastic in which it could be dispersed at the molding temperature of the nylon MXD6 (272°C). The system could also be used in any low oxygen permeability plastic with which it were compatible. The limit in oxygen permeability for the effective structural plastic is in the range of five times that of PET (PET P=5), but not much more. The system has been tried in polypropylene (P=150) (Adams, 1991) in a multilayer structure including polyester skin and the nylon MXD6 oxygen absorber system. The developers reported that the introduction of the oxygen scavenger system reduce the oxygen permeation a substantial two orders of magnitude, from a factor of 60 to 300. The final oxygen permeation was reported to be less than 2 cc O₂/m²/atm/day. Among the multilayer structures suggested are, from the outside, OPET/polypropylene, nylon MXD6, and cobalt/polypropylene as the heat sealant layer. This sheet structure was intended for thermoforming into cup-shapes probably suitable for retorting. Also, the nylon MXD6 limit of about 5% is important from an economics perspective.

PET costs about US\$0.70 pound, while the nylon MXD6 is \$3.00/pound. At the 2% weight level, including \$0.05/pound for blending, the cost of the mixture to make Oxbar™ would be \$0.80/pound, which is \$0.10/pound more than PET alone. Although

other nylons have been used, only MXD6 appears to function effectively. The patents, however, are for any oxidizable polymer.

It should be noted that this system is specific for oxygen and does not function for other gases or vapors, which is true for almost all scavengers, including iron oxide. Flavor loss due to absorption and CO₂ permeation would be the same. The Oxbar™ scavenger system does not depend on moisture, which is another potential benefit unless one of the purposes of the scavenger is to remove small quantities of moisture.

At the 2% by weight level, the clarity with PET is good; however, as the MXD6 content increases, transparent materials become gray. Applications to date of the 2% by weight level system would be used in any product that could be packaged in PET with high oxygen barrier requirements.

In 1991, Continental PET Technologies in the United States received a patent for multilayer transparent bottles containing a blend of polyester and nylon MXD6, and of polyester, nylon MXD6 and cobalt (Collette, 1991). The nylon MXD6-containing oxygen scavenging system is present only in the core layer of the multilayer bottle, which is coinjected with conventional bottle grade polyester in order to reduce the overall bottle percentage of nylon MXD6 to less than 1% by weight. The MXD6 constitutes 25+% of the core layer blend which, in turn, constitutes about 4% of the total injection molded perform or bottle. At this level, the developers reported clarity in both injection molded preforms and in final bottles blown from the preforms.

The current U.S. FDA attitude is towards permitting approval for materials with potential migration problems. Thus, if the blend is separated from the interior contents by at least 0.001 inch of virgin barrier plastic, it may be possible that this structure would not encounter the same regulatory questions as previous versions. This interpretation, if valid, might not be applicable for film formation because of the thinner gauges.

No data were reported on the oxygen permeability of the multilayer structure, and so the oxygen removal benefits of this system are only speculation. The Oxbar™ concept has sufficient merit to warrant further investigation, and perhaps may be the most promising of all those approaches suggested in this review of world technology.

A variation of the nylon MXD6/cobalt blend as an oxygen scavenger received a 1993 United States patent (Frandsen et al., 1993) assigned to Danish package material converter A/S Hastrup Plastic. In this system, the polymer and the metal were refluxed together (using alcohol) to obtain a combination of the nylon MXD6 and the metal which were then pelletized. The pellets, being active oxygen absorbents, were presumably placed into sachets and then into sealed packages from which the oxygen was removed. Oxygen in sealed metal cans was reduced from 0.3% to 2.5% after four

weeks at ambient temperature.

D. Aquanautics/Advanced Oxygen Technologies (AOT)

Advanced Oxygen Technologies, Inc., formerly Aquanautics Corporation, is a company with current financial difficulty (as of this writing). Their well-published scavenger products are a series of oxygen-binding complexes marketed under the trade name SmartMix® for applications that include the removal of trace residual oxygen from beverages. These compounds, organo-metallic ligands, function in a fashion similar to that of hemoglobin, which transports oxygen in blood; however, the AOT products have been reported to be simpler, synthetically-produced molecules. A number of these complexes have been immobilized on insoluble supports in functional package material form. These immobilized oxygen binders have been demonstrated to be effective at reducing oxygen levels from aqueous solutions, including beer, to as low as 10 ppb. They can be used as part of the package itself, such as the closure, to remove oxygen from the product through the headspace. In addition, the company claims they can incorporate the materials into plastic film and sheet form.

Proof of the scientific principle of ligands has been demonstrated in the form of oxygen binders immobilized on silica and other supports. These reductions to practice resulted in the engineering and production of commercial oxygen absorbing systems for application in the food and beverage industries. The term "ligands" refers to small molecules used for oxygen binding and absorption.

Target applications to date appear to be liners for closures for beer, wine and fruit juice bottles and other oxygen-sensitive foods and beverages. The initial target for the closures is the beer industry, with the first commercial reduction to practice having been beer. These closures are produced and marketed by bottle closure producer Zapata of Hazleton, Pennsylvania.

The initial objectives of AOT's developments were to:

1. Develop an immobilized insoluble oxygen scavenger with a capacity for binding O_2 on the order of 5 cc (220 μ moles) per gram of scavenger;
2. Develop a prototype bottle closure liner incorporating the scavenger, capable of deoxygenating beer to less than 50 ppb (0.01 cc in 12 ounces) by selectively binding the O_2 present in both the headspace and the beverage;
3. Perform pilot testing of the bottle closure for application in the beverage industries.

The technology developed by Aquanautics is unique in that oxygen is tightly bound

rather than chemically reacted, which has the important effect of not creating additional by-products or a partially-reduced oxygen species which may cause off-flavors.

The most widely known oxygen carrier is that found in nature, i.e., hemoglobin. AOT claims the ability to "mimic" this complicated "heme" O_2 carrier by the development of a number of oxygen carrier complexes based on the fundamental structure shown in Figure 1. Since these chemical structures are very water soluble and have relatively limited use in beverages, a major effort was launched to immobilize and thus insolubilize them maintaining their inherent oxygen binding ability. AOT claimed success in accomplishing this task which is shown schematically in Figure 2. The immobilized O_2 scavenger retains high affinity for oxygen, and has been demonstrated to be able to remove oxygen from aqueous solutions down to less than 50 ppb. This immobilized structure is the basis of the SmartMix® oxygen scavenging system.

Beer crowns containing immobilized SmartMix® have been used commercially on 12 ounce beer bottles by a number of smaller brewers such as G. Heileman Brewing Co. and tested by major brewers such as Anheuser-Busch and Miller. AOT reported that after the first 24 hours, the oxygen concentration was reduced to less than 50 ppb from an initial concentration of over 2000 ppb.

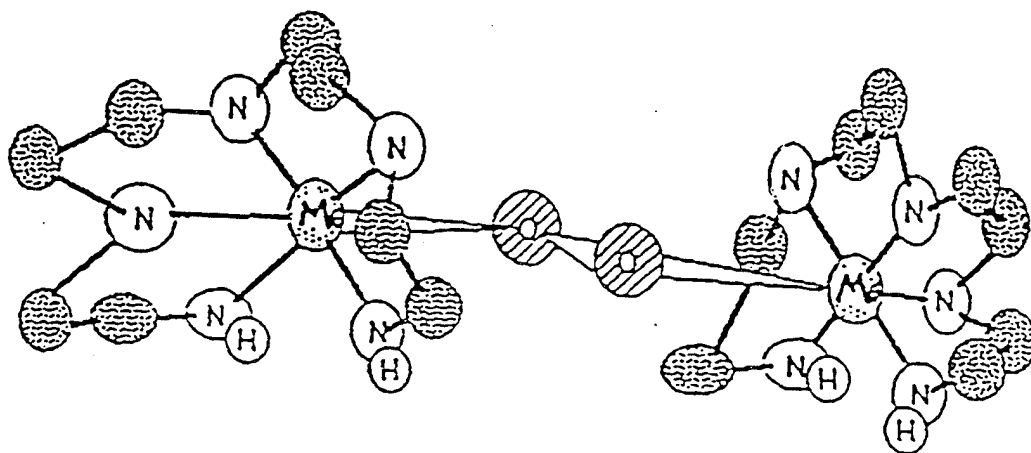


Figure 1. Ligand/Metal Complex Shown Binding Oxygen

The experiments demonstrated that when the oxygen scavenger is not in direct contact with the beer, it is effective in removing oxygen from the beer. As the oxygen is removed from the headspace, which accounts for about two-thirds of the total small quantity of oxygen in the bottle according to AOT, dissolved oxygen vaporizes from the liquid into the headspace to re-establish equilibrium. This additional oxygen was then scavenged, and this process continued until only a trace amount of dissolved oxygen, less than 50 ppb, was left.

A major issue in the commercialization of an oxygen scavenging closure was the activation of the scavenger after closing the bottle. The experiments demonstrated that, while admixed scavenger material is inactive at normal ambient temperature and relative humidity conditions, when the cap is subjected to the high relative humidity conditions of the headspace, scavenging takes place. Increasing the temperature, as in the beer pasteurization cycle, activates the scavenger and increases the rate of scavenging.

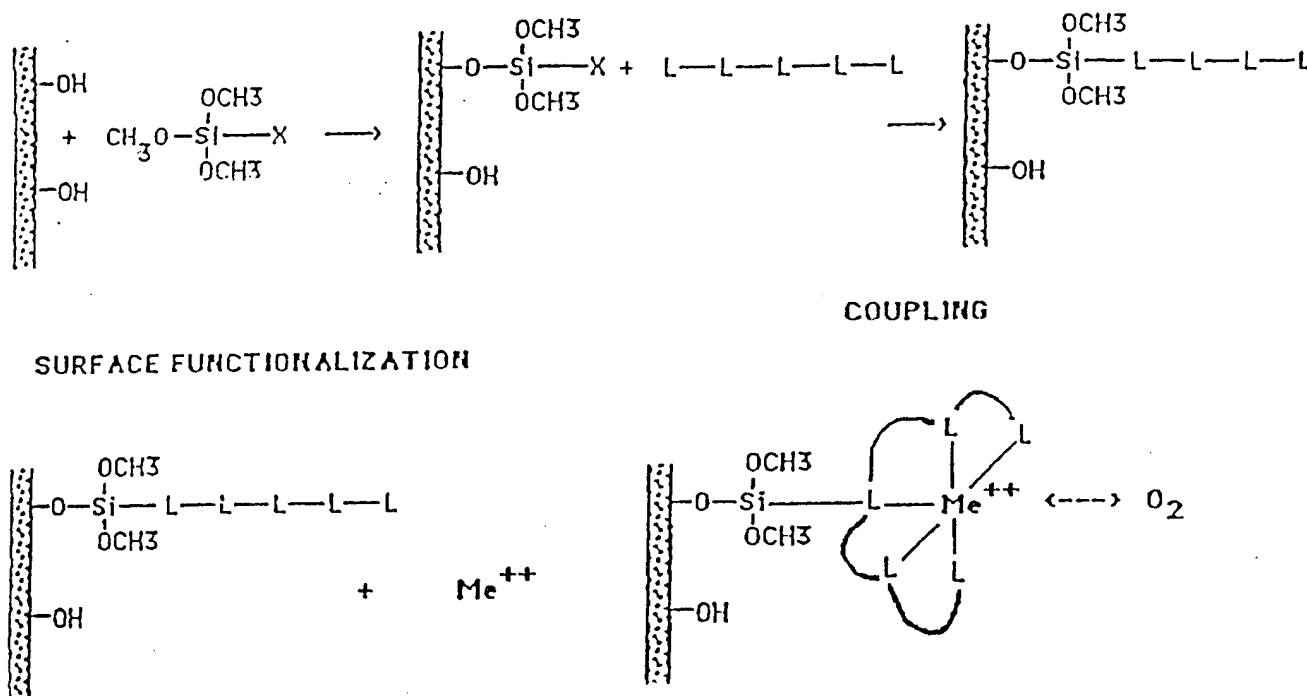


Figure 2. Schematic Representation of Immobilization and Activation of AOT's Scavenger on a Silica-Based Insoluble Support Structure (Activation by Divalent Metal Ion)

The AOT product is meant to be added to a polymeric system such as a closure liner where it can perform one of two, or both, reactions: scavenge the traces of oxygen that might be left in the headspace and/or capture oxygen as it diffuses through the wall from the exterior air.

The particular materials being used for AOT's system are reported by them to be non-toxic and evidently have current U.S. FDA generally recognized as safe (GRAS) status since they are being used.

Although encouraging from apparently all perspectives, progress is considerably slower than projected in the public announcements. Early testing with Anheuser-Busch for beer proved less than satisfactory due to the additive causing off-flavors in the very flavor-sensitive beer. These "off-flavors" may have actually been the base flavors of unoxidized beer that were previously unknown in beer. Previously, all beer exhibited minute oxidation flavors which are obviated by the presence of the oxygen absorber. Some observers feel that these flavors may actually be desirable to consumers. After the resolution of these problems, commercial quantities of beer using the AOT technology in the closures from small brewers appeared in the marketplace.

AOT has incorporated their scavenger into the liners of aluminum roll-on closures for glass bottles and into plastic resin for molding into bottles; they also have spotted their scavenger into the liners of aluminum beer can ends.

The AOT technology is sufficiently different from other oxygen scavenging technologies to warrant a more detailed description.

The extraction of a small ligand such as molecular oxygen requires a ligand carrier compound immobilized on or in a solid phase. The carrier compounds contact the oxygen-containing environment to extract the ligand. The carrier compound consists of a transition metal complex including a transition metal ion and a multidentate organic chelate. The solid phase is separated from the oxygen-containing environment and may be in the form of discrete particles, sheets and films in which the organic chelate is covalently attached or non-covalently adsorbed to the solid phase. Alternatively, the carrier compound may be physically retained within a solid phase comprising a ligand-permeable membrane that is not attached at the molecular level. The multidentate organic chelate may be polyalkylamines and the transition metal may be ions, e.g., manganese, chromium, iron, cobalt and nickel.

Multidentate organic chelates are unable to bind oxygen when they are not complexed with the transition metal ion. Thus, the materials may be initially formed with the transition metal ion segregated from the organic chelate. The organic chelate may be mixed with the transition metal in the form of a metal salt. As long as the mixture is maintained in a dry state (e.g., relative humidity below about 50%), the transition metal is unable to combine with the organic chelate, and the mixture remains inactive. By exposing the mixture to sufficient moisture, however, the transition metal and the organic chelate are able to combine to activate the composition.

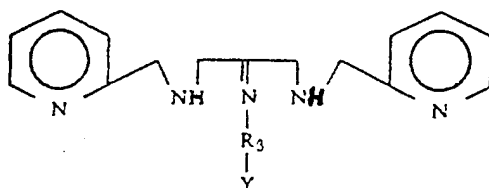
Typically, the immobilized carrier compounds (in either active or inactive form) are retained behind or within a gas permeable membrane. The membrane is incorporated into the packaging and is able to absorb oxygen after sealing the package. The membrane may be in the form of a discrete packet, which may be placed in a larger package. The membrane may also be incorporated into the package, such as within a

bottle closure. In either case, oxygen passes from the interior of the package through the membrane to the absorbent to be captured.

For oxygen binding, the transition metal is usually manganese, iron or cobalt. The primary requisites of the transition metal are that it form complexes, and that it has a first valence state in which the transition metal complex binds molecular oxygen. In known transition metal complexes that will be suitable for use, the valence state in which oxygen is reversibly bound will be lower (more reduced), e.g., Mn(II), Fe(II) Co(II) or Cu(I). Transition metal complexes can be formed from a variety of multidentate (multicoordinate) chelates, especially tetradentate and pentadentate chelates. Multidentate organic chelates may be macrocyclic, branched or linear.

The carrier compounds may further comprise various monodentate, bidentate and tridentate chelates including nitrogen bases such as ammonia, amines, amino acids and their derivatives. The chelates are normally combined with other chelating molecules to form multidentate carrier compounds. Thus, not all ligating molecules in the multidentate structure must be covalently bound to one another. Examples of carrier compounds comprising a tetradentate molecule combined with a monodentate molecule include pentadentate chelates such as polyalkylamines.

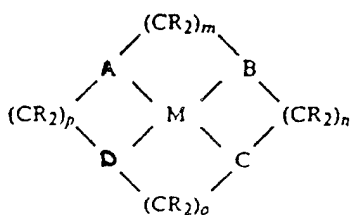
Useful polyalkylamines are generally linear and pentadentate. At least four of the atoms that are available for coordination to the selected transition metal ion (generally referred to as "ligating atoms") are nitrogen atoms. The remaining ligating atom is usually the third or central ligating atom and is typically nitrogen or oxygen. The ligating nitrogens may be of the primary, secondary or tertiary aliphatic or aromatic type, and more than one type of nitrogen may be present in the same polyalkylamine. Ligating oxygen, when present, will usually be of the ether type. Representative useful polyalkylamines have the general formula:



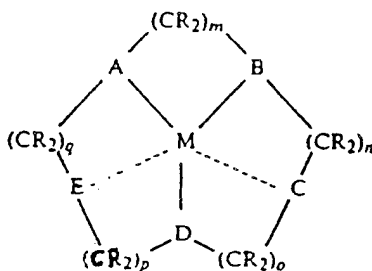
where R₃ is lower alkylene, preferably being ethylene, propylene or butylene, and Y is a chemically reactive functional group, such as amino, vinyl, carboxyl, acid and chloride.

A second class of multidentate organic chelates that are useful to form the transition metal carrier compounds comprises macrocyclic amines, including tetradentate, pentadentate, and hexadentate. The macrocyclic amine chelates useful in

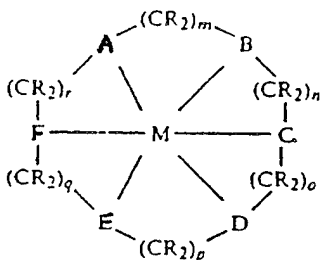
the development include those of the general formulas:



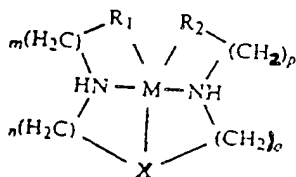
and;



and;



Particularly suitable ligand carrier compounds are metallic complexes composed of pentadentate polyalkylamines, which have the following general formula:



The solid phase may be in the form of particulates, beads, powders, sheets and films and may be materials such as silicas, zeolites, polymer beads, microporous glass beads, celluloses, polysaccharides and polymer films. Particulates which meet these

requirements include silicas because of their low cost and high surface area, which affords maximal loading of the carrier compounds. The preferred sheet materials may be oxygen permeable or impermeable depending on the desired application. Oxygen permeable polymers such as silicone rubber, polybutadiene and polyvinyl acetates are useful when it is desired to allow oxygen penetration and when it is desired to absorb or entrap the oxygen within or on the surface of the sheet material. Oxygen barrier polymers such as polyethylene terephthalate (PET) are useful when it is desirable to form packages or other structures which resist oxygen penetration. The carrier compounds may be attached to the surface or incorporated within such polymers to scavenge any residual oxygen.

The carrier compounds or organic chelate are adsorbed or covalently attached to the surface of the solid phase; or they will be immobilized or retained within the solid phase, i.e., the solid phase is a ligand-permeable barrier which physically traps the carrier compound or the organic chelate. Alternatively, the solid phase may be a matrix formed by polymerization of a monomer in the presence of the carrier compound, or at least the multidentate organic chelate, under conditions such that the carrier compound is embedded in the resulting matrix. Such polymers may be prepared by free-radical, ionic or heterogeneous polymerization mechanisms such as derivatives of acrylamide, acrylic acid and methacrylate and polymers such as Surlyn® ionomer.

Covalent surface attachment is the preferred type of immobilization when the loss of carrier compound from the composition is undesirable. Covalent surface attachment are also generally employed with inorganic solid phase materials such as silica and alumina particulates as well as glass beads.

Incorporation of the carrier compounds into rigid or flexible polymeric sheet materials can be accomplished by a variety of techniques. For example, the carrier compounds may be mixed with a resin and the mixture extruded to form a single-layer sheet or film by conventional manufacturing techniques. Alternatively, the carrier compounds may be combined with a plastic resin and the combination coextruded or coinjected with another resin to form a multilayer sheet/film or bottle/jar. The layer containing the carrier compounds may be on one side of the structure or may be sandwiched between plastic layers which are free from the carrier compounds. It is also possible to combine the carrier compounds in two or more of the layers that are coextruded. The carrier compounds also may be combined in a coating material that is applied to the plastic sheet or film after the sheet or film has been fabricated.

Monolithic polymeric sheets, films and other structures may be formed by conventional plastic manufacturing techniques, typically extrusion and injection molding. The carrier compounds may be activated at the time of incorporation (i.e., may be in an active form with complexed transition metal ions) or may be inactivated (free from complexed transition metal ions). In the latter case, the transition metal ions can be

introduced later to provide active carrier compounds.

The multilayer polymeric structures may be formed by coextrusion or coinjection of the different desired material layers. Such coextrusion or coinjection processes are utilized to combine, for example, EVOH or polyvinylidene chloride (PVDC) with polypropylene layers. The carrier compounds could be employed in one or more of the multiple layers produced. In some cases, it might be desirable to provide individual layers which are oxygen permeable and other layers which are oxygen barriers. By then incorporating the carrier compounds in the oxygen permeable layers, they function as oxygen absorbent layers that scavenge the oxygen that penetrates the oxygen permeable layer(s).

Coating formulations incorporating the carrier compounds may be provided for virtually any type of material, plastic or otherwise.

In use, the total amount of oxygen absorbing capacity of the immobilized carrier compound must be greater than the amount of oxygen that can reasonably be anticipated to be contained in the environment from which oxygen is to be extracted. Preferably, the amount of oxygen absorbing capacity is 3 to 10 times greater than that which can reasonably be anticipated to be extracted.

Typically, oxygen-absorbing structures may be formed to allow selective activation based on exposure to water or other polar solvents of an immobilized chelate. Such structures generally employ membrane barriers that initially maintain the carrier compounds and transition metal ions in an uncombined state, typically with the transition metal in the form of a salt. Conveniently, the organic chelate and transition metal salt are combined in a dry form so that the chelate and the metal ion are unable to form a complex until exposed to water. Complexes are formed by exposure of the dry chelate and salt to a wet ligand-containing environment, such as a beverage. Alternatively, the water may be present in the oxygen-absorbing structure but isolated from the chelate and salt, typically by microencapsulation of the water. Combination of the ion and the chelate may then be effected by physically rupturing the microencapsulation. By performing all package fabrication and filling operations in a dry environment, the oxygen absorbent remains in its inactive state. Activation occurs after sealing as a result of exposure to water in the package.

Membranes such as silicone rubber that are suitable for use in such packaging structures are gas permeable, but possess sufficient mechanical strength to contain the oxygen-absorbing compositions.

In some cases, it may be desirable to use membranes capable of providing a selective barrier to oxygen. With such membranes, premature ligand binding could be avoided even when the oxygen absorbent compositions are in an active state, i.e., with

the transition metal ion bound to the multidentate organic chelates.

Alternatively, it sometimes may be desirable to utilize membranes which are moisture permeable only when heated. Such membranes would allow package fabrication and filling operations to be performed in moist environments, without premature activation of an absorbent incorporated behind the membrane. Such membranes, however, are generally only useful with products that are not degraded at the temperatures required for activation of the absorbent materials.

It may be desirable to incorporate the membrane structures into a package closure. In this way, the oxygen absorbent material may be activated immediately prior to or after package sealing allowing maximum oxygen absorption capacity. By incorporating the oxygen absorbing materials in the package closure, the remaining portion of the package can be filled with product without regard to premature consumption of or activation of the absorbent material. Such closure structures are useful when employing moisture-activated absorbents where a packaged liquid will be available to activate the absorbent after the package is closed. In this way, activation does not occur until after sealing.

The cost of the SmartMix® material was reported by AOT to be US\$50 per pound, which is expensive, and can add from 2% to 15% to the total package costs. The oxygen scavenging capacity of these materials is about 1-2 cc O₂ per 1% load of SmartMix® per gram of polymer.

In addition to their series of ligand developments, AOT also conducted research on chelating agents as oxygen scavengers. These materials can be dispersed in plastics and are claimed to have relatively high oxygen scavenging properties.

The oxygen scavenging material is a transition metal complex or chelate of an organic polycarboxylic acid, e.g., amino polycarboxylic acid such as ethylene diamine tetra acetic acid (EDTA) or its salt. It is also possible to employ other polycarboxylic acids such as citric and oxalic acids, which are capable of forming a chelate with the transition metal. Such polycarboxylic compounds may contain one or more amine, hydroxyl, carboxylate or sulfhydryl groups. Preferably, the transition metal is iron or copper in the form of a simple chloride, sulfate or gluconate salt. A reducing agent, such as an ascorbate compound, may be included in the polymer to augment the oxygen scavenging properties of the chelate. Preferred carriers include polyolefins, PVC, polyamides, EVA and PET.

The preferred polymers, which may be used as the carrier, are water vapor permeable so that exposure to elevated temperatures is not necessary to activate the oxygen scavenging capabilities of the composition. The oxygen scavenging material is uniformly dispersed in and throughout the polymer by a direct mixing technique. The

oxygen scavenging capabilities of these materials are later activated by contact with water or water vapor, which permeates into or through the carrier.

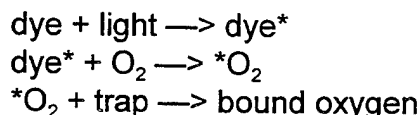
The oxygen scavenging material may be present on an inside surface of the package, may be dispersed relatively uniformly throughout the film, or may be in a multilayer film with the oxygen scavenging composition present in one of the layers. The oxygen scavenging composition can be applied as a coating or lining upon the inside surface of the package structure. Another application, of course, is in the form of a bottle closure liner or of a can end compound.

E. Photosensitive Dyes

Australian researchers from Commonwealth Scientific and Industrial Research Organizations (CSIRO) in North Ryde, New South Wales, Australia have published extensively on chemical systems for oxygen scavenging. One of their systems used photosensitive dyes in conjunction with other compounds that react with the singlet oxygen formed by these dyes on illumination. They have suggested that when oxygen is excited to the singlet state, the reaction is much faster than with iron compounds because the latter is a ground-state oxygen reaction.

One process utilizes reactions inside the packaging film containing a photosensitizing dye and an excited oxygen trap. On illumination of the exterior of the film with visible light, dye molecules become excited and pass their excitation to oxygen as it diffuses into the film from either the package headspace or out of the liquid food. The excited oxygen molecules react with the trap and become bound, i.e., are scavenged. While the film is illuminated, the process continues until all the oxygen or trap (oxidizable constituent) is reacted.

The reaction scheme is:



where * represents an excited state of the species.

This photochemical process offers advantages over most of the other oxygen removal processes because it requires no addition of sachets to the food package, does not involve particulate matter in the transparent packaging material, and its rate can be controlled with light. However, scavenging does not occur in the dark and so a good oxygen barrier plastic in place of aluminum foil would be necessary for highly sensitive foods.

A small pouch lined with a scavenger film area of 150 cm² and containing 25 ml of air can be deoxygenated in about 15 minutes.

In this CSIRO process, a photosensitive dye is impregnated onto ethyl cellulose film. Upon exposure to visible light the dye activates oxygen to the singlet state. This oxygen then can react with any acceptor to form an oxide. The dye first used was erythrosine. The singlet oxygen acceptors tested were difuryllidene pentaerythritol (DFE), tetraphenyl prophine (TPP), dioctyl phthalate (DOT) and dimethyl anthracene (DMA), but these are not FDA approved for food contact.

Ascorbic acid was also tested as the oxidizable substance in combination with the photosensitive dye. One advantage of ascorbic acid is that it does not trigger a metal detector on line. The U.S. FDA status of the dyes noted is as unregulated additives; but it is possible that they may be allowed in some packaging material if a functional barrier exists to prevent their migration into food. The Australian work shows the rate of oxygen scavenging to be dependent on the extent of exposure to visible light, which means that the process could be ineffective in some opaque packages or containers. The second limitation is oxygen permeation into the film. In all cases, the oxygen was scavenged from 30 ml of headspace in 30-80 minutes, with the rate slowing down after the level reached 2% oxygen. The rate follows first order kinetics.

The polymer system has been improved to bind the reaction products as part of the package to prevent migration into the food. The initial work involved dissolved reagents. Subsequent work involved development of a polymeric furan to trap singlet oxygen.

A 1994 international patent application from CSIRO describes a quite different oxygen scavenging process that functions independently of transition metal catalysts (Rooney, 1994). The system contains a reducible organic compound that is reduced under predetermined conditions. The reduced form of the compound is oxidizable by molecular oxygen so that its reduction and/or subsequent oxidation occurs independently of the presence of a transition metal catalyst. The reduction and/or subsequent oxidation of the one reducible organic component is also independent of the presence of an alkali or acid catalyst. The reducible organic compound may be reduced under predetermined conditions such as by exposure to light, heat, gamma or electron beam irradiation, or corona discharge. The compound possibly may be reduced by incorporating a reducing agent which in turn can be activated by heating.

Typically, the reducible organic compound has the capacity to be converted to an excited state such as a triplet form. The triplet form then becomes reduced to an essentially stable state by gaining or abstracting an electron or hydrogen atom from other molecules, or by redistributing an electron or hydrogen atom within the compound itself. The reduced molecule is reactive towards molecular oxygen to produce activated

species such as hydrogen peroxide, a hydroperoxy radical or a superoxide ion. Preferably, the reducible organic compound should be stable in air at room temperature or should be in its fully oxidized state. Examples of such compounds include substituted anthraquinone, such as 2-methylantraquinone, which can absorb in the UV spectrum. The reducible organic compound component may constitute up to 50 percent by weight of the material. In practice, these simple anthraquinones would be replaced by high molecular weight derivatives.

Compositions that involve the formation of an activated oxygen species, e.g., peroxide, may further consist of a scavenging component reactive towards the activated species. The suggested scavenging component is an antioxidant, such as BHT or BHA.

The activated oxygen species-scavenging component may be in the form of a polymer or oligomer. Such forms may be prepared by, for example, covalently bonding a compound, such as those activated oxygen species-scavenging compounds, to a monomer or co-monomer.

As an alternative to components that can be excited to a state that converts oxygen to an activated species, components may be used that are excitable to a state in which they react and bind directly with entering oxygen.

Preferred polymers include vinyls, polyolefins and polyesters, or include their copolymers, ethyl cellulose and cellulose acetate. Heterogeneous substrates, e.g., in organic polymers such as silica gel or polymer mixtures, may also be used.

Alternatively or additionally, the reducible organic compound itself may be in a polymerized form either as a homopolymer or copolymer. Reducible monomers can be made by covalently bonding an ethylenically unsaturated group to a reducible organic compound. The reducible organic compound may also carry groups capable of reaction with other polymerizable molecules and preformed polymers. Examples of ethylenically unsaturated reducible monomers include vinyl derivatives, preferably bonded to the reducible organic compound in such a manner as not to decrease the lifetime of the triplet excited state.

Co-monomers can be any ethylenically mono-unsaturated or polyunsaturated substance such as vinyl acetate, vinyl alcohol, acrylonitrile, methacrylonitrile and acrylic monomers.

Reducible monomers may be polymerized as condensation polymers such as polyesters or polyamides.

When the reducible organic compound is in a polymer that does not readily donate

a hydrogen atom or electron to the reducible organic compound in its excited state, an additional source of labile hydrogen or electrons is preferred for use. Such a compound is preferably one containing a hydrogen atom bonded to nitrogen, sulfur, phosphorous or oxygen. Other sources of electrons are salts of organic compounds, such as the salts of sulfonic or carboxylic acids. In one form, the sodium sulfonate salt of a polymerized 9,10-anthraquinone would be used. Thus, the reducible organic compound itself can be the source of its own electron for the reduction process.

The reduced form of the organic compound used brings about a reduction in the molecular oxygen concentration in the environment or liquid contents. The rate of reduction and/or oxidation is independent of the presence of a transition metal, alkali or acid catalyst. Nevertheless, transition metal compounds, alkaline and/or acidic agents may be included when they may affect the rate of oxygen scavenging or may enhance the reduction and/or subsequent oxidation of the organic compound. For example, ascorbic acid may be included in the materials containing anthraquinones as a photoreduction enhancer.

Reduction of the organic compound may take place as required: when the material is being converted into or brought into contact with a package material, but prior to filling and sealing. Reduction may even be deferred until after sealing the package.

The compositions may be used independently or as components of blends. They may take the form of a cross-linked polymeric matrix, as in a can lacquer, or they may be bonded to or absorbed onto an inorganic polymer, such as silica. They may be applied as, or incorporated into, bottle closure liners, PET bottles, inks, coatings, films or sheets, either alone or as laminations or coextrusions. They also may take the form of pads, spots, patches, sachets, cards, powders or granules that may be attached to the packaging material or are located independently within a package.

Films may be monolayer or multilayer laminations and may be used on their own. When the film is a multilayer, an outer layer should be an oxygen barrier so that the film may be used with only the layer(s) containing the reducible organic compound exposed to molecular oxygen from the atmosphere.

Films comprising the material may also be used as a chemical barrier to oxygen transmission through a packaging material. Thus, the oxygen passing through from the outside environment into a reduced oxygen content atmosphere within the package can be scavenged by the reducible organic compound. The composition can be dissolved or dispersed within the packaging material, or can be placed adjacent to the material as an additional layer on the inside of the package.

In multilayer laminations, an activated oxygen species-scavenging component may be provided in a separate layer from the layer comprising the activatable component.

Film layers containing a reducible organic compound may be formed either by extrusion or by casting. The layer comprising the reducible organic compound may be extruded onto another substrate as in extrusion coating and lamination.

The blends may, if necessary, be re-reduced by resubjecting them to the pre-determined activation condition if they have been exposed to air prior to package sealing. Re-reduction may be achieved at a light intensity as low as ambient room illumination.

The technologies can be self-indicating, i.e., upon reduction some reducible organic compounds undergo a change in color or change in UV-visible, infrared or near-infrared absorption spectrum. For example, photoreduction of quinones and some of their derivatives results in a spectral shift from the UV to longer wavelengths, especially to the visible region of the spectrum. Thus, a package material can be formulated to undergo a color change as the capacity for reducing the oxygen concentration becomes exhausted. This color change also provides a mechanism for checking whether or not all of the reducible organic compound in the composition has been reduced. The color change may be used as an indicator of seal compromises.

Among the many examples cited were:

1. Photoreduction of 2-methylantraquinone in ethyl cellulose sandwiched between two layers of polyvinylidene chloride-coated polypropylene: 2-methyl anthraquinone was dissolved in ethyl acetate together with ethyl cellulose, and a film was cast of 20-30 micrometers gauge. This film was placed between two layers of the PVDC-coated polypropylene, and the two outer layers were heat sealed together to form a flat package with essentially no headspace containing the ethyl cellulose layer. The three layer sample was exposed to the light from a xenon lamp.
2. Photoreduction of 2-methylantraquinone in ethyl cellulose sandwiched between a layer of Surlyn ionomer and a coextruded film of Surlyn/ethylene vinyl alcohol copolymer/nylon 6: A sample of the ethyl cellulose film was placed between one high-permeability layer, Surlyn and one low permeability coextruded layer containing ethylene vinyl alcohol as the barrier. The sandwich was illuminated so that the quinone was photoreduced.
3. Scavenging oxygen from air in pouches made from a high oxygen barrier plastic: Two-methylantraquinone was dissolved in ethyl acetate, together with ethyl cellulose and a film cast on the Surlyn ionomer side of a coextruded film. A pouch made from this film was flushed with nitrogen and exposed to xenon lamp irradiation, and then was stored in darkness. The film has an oxygen transmission rate of 6 cc/m²/day at 20°C. The oxygen concentration could be

reduced to as low as 0.07%.

4. Oxygen scavenging by 2-methylantraquinone in a UV-cured varnish: A mixture of a commercial UV-curable varnish and ethanol was used to dissolve 2-methylantraquinone. This mixture was applied to a polypropylene film as a 2-3 μm thick layer. After nitrogen flushing, the pouches were exposed to xenon lamp irradiation. Up to half of the oxygen present could be removed.
5. Oxygen scavenging from a tinplate steel can: A crosslinkable polyurethane resin was used to demonstrate the use of an oxygen scavenging coating on the inside of a tinplate steel can. A 465 ml can was coated internally with a solution containing 2-ethylantraquinone and triphenylphosphite in ethanol. The can was then exposed to irradiation and closed by double seaming. The headspace gas was analyzed after 24 hours by which time the oxygen concentration had been reduced from 20.6% to 19.5%. The oxygen consumed was 2.5 ml, representing the quantity of oxygen which can be found sometimes in commercial cans.
6. Reducible organic compound: Copolymers of 2-vinylantraquinone were made with styrene and with 2-hydroxyethyl methacrylate. Films were cast on the polyester/ EVOH/Surllyn ionomer barrier film. The films were made into pouches that were irradiated. Test results showed that the polymers scavenge oxygen, but their permeability to oxygen can result in slower scavenging than with a highly permeable film such as ethyl cellulose.

F. End Product Scavengers

Aldehyde scavengers, not oxygen scavengers, are the materials proposed and tested by DuPont to remove the undesirable end products of food product oxidation (Brodie, 1994). DuPont's initial development work has been mostly aimed at removing undesirable components from the inside of the package. DuPont's initial work used polyethylene-imide to scavenge aldehydes, such as hexanal and heptanal, formed from oxidations of fats and oils. These aldehydes can cause rancidity, off-taste and off-odor to a food product. A master batch containing the aldehyde scavenger can be incorporated into a number of different flexible package structures, such as a non-barrier or barrier coextrusion for food products such as snacks, crackers, cookies and cereals.

The scavenger can be incorporated into a small pouch containing a coupon that would then be inserted into a larger bag. The scavenger can also be incorporated into the actual coupon or into membrane lids and cap liners. Incorporation into the membrane lid between the barrier layer and the sealant layer into plastic used in a cap liner is suggested. Inclusion in one of the layers of a multilayer plastic container is also proposed.

Laboratory tests on aldehydes in the package headspace were run on actual food products after exposing the packaged products to 46°C. Results obtained on peanut butter comparing no scavenger in the lid to two levels of aldehyde scavenger demonstrate the effectiveness of the scavenger, particularly at the higher level, in removing aldehydes from the headspace. Results obtained on a powdered coffee creamer after four weeks showed the scavenger is extremely effective at the higher level.

Test results for the presence of hexanal in the headspace of a snack product package show significantly less hexanal in the headspace of the bag containing the scavenger at the end of the product's normal shelf life. The hexanal in the package headspace was only half that of the standard package. Tests on instant coffee after 12 weeks of exposure show significant reduction in total aldehydes with both levels of the aldehyde scavenger.

CONCLUSIONS

Protection of packaged food contents for extended periods requires that the product itself must be processed and packaged to stabilize it against biochemical activity and, in particular, oxidation. Even when the package is a high gas barrier structure that is hermetically closed, the seal is not a route for gas transmission into the package. Except for intact metal or glass, package materials permeate oxygen. As much as mechanical vacuum and gas flush systems reduce oxygen in the headspace, they do not eliminate it. Further, products often contain occluded or dissolved oxygen which is reactive with the product.

Recognizing that residual oxygen reacts biochemically with contained food and causes entering adverse oxidative effects, barrier and vacuum packaging have been supplemented in recent years by post-packaging oxygen removal.

Although several technologies to actively remove scavenging oxygen from package interiors were reported in the 1940s, experimental testing dates only to the 1950s and commercialization only to the late 1970s. When Japan's Mitsubishi Gas Chemical inserted reduced iron powder-containing gas permeable sachets into packages of foods in 1977, oxygen scavenging began to be known as a commercial technology to help protect contained foods against oxidative deteriorations.

Only one United States' company supplies domestically manufactured oxygen scavengers, and four viable United States' companies have active oxygen scavenger development programs.

A major producer of internal package desiccants, Multiform Desiccants, Inc. began production of reduced iron-based oxygen scavenger sachets during the late 1980s. They probably remain second in commercial volume to the imported Ageless® product in the United States. Their developments have led them to a flat label form, which is currently being used for cured meat packaging in the United Kingdom, and probably will be translatable into package form in the future.

Advanced Oxygen Technologies' program (formerly Aquanautics) was based on U.S. Navy research on artificial gills for underwater activities. Their scavenging product has been incorporated into plastic liners for the interiors of metal closures for beer bottles. The application has been by bottle closure manufacturer Zapata. A very disappointing commercial result to the product launch has been, in part, responsible for AOT's present financial difficulties. Commercial applications during the 1990s have been among boutique brewers which constitute only a very small market.

Amoco Chemical Company's developmental activities during the 1990s apparently

began with materials to incorporate into rigid plastic packaging structures, and not sachets.

During the late 1980s, Carnaud MetalBox in the United Kingdom developed and introduced jars and polyester beverage bottles that contained small quantities of nylon MXD6 plus cobalt as a catalyst to react with oxygen. This technology, called Oxbar™, was demonstrated to be a very effective oxygen scavenger or interceptor; but Oxbar™ did not receive regulatory approvals, which is one reason that the company severely truncated its activity in this technology. Oxbar™ is one of the few oxygen scavenging technologies proposed in which the technology is incorporated directly into the package material itself, although in this case, it was semi-rigid containers.

1. Commercial Applications

Current commercial applications for reduced iron oxygen scavengers in sachets, which is almost the only type used in the United States, are surprisingly limited. The largest single use is for fresh pasta, with all other uses being relatively small and dispersed among a variety of applications.

In Japan where the annual market is probably in excess of two billion sachets and growing, commercial applications include insertion into packages of soft bakery goods, dry snacks, dry cured meats and candies. This relative success may be due to the early commercial introductions, the greater desire for long-term distribution and the lower concern about cost.

In Europe, the major commercial application may be for W.R. Grace's liners for beer bottle closures. Outside of Japan, i.e., in Europe, oxygen scavengers have not demonstrated commercial success.

This paucity of commercial success in all parts of the world except Japan has occurred in spite of the proven and well-known commercial efficacy of the product.

2. Oxygen Removal Chemistries

In-package oxygen scavengers of consequence either in commercial use or proposed for commercial development include:

1. Unsaturated linear hydrocarbons: They can be relatively easily blended into polyolefin plastics, and apparently represent a family of oxygen scavengers being actively studied as package material constituents by both W.R. Grace & Company and Mitsubishi Gas Chemical.
2. Reduced iron salts: By far the mostly widely used commercially, they have ex-

cellent oxygen absorption capacity and scavenging speed. They require moisture to function, which may be obtained from the evaporation of content water or from a water-emitting compound in the dry mix. Problems include: uniform dispersability; color when incorporated into a plastic sheet or film; finite capacity; and cost, which although relatively inexpensive compared to other oxygen scavengers, still adds to the cost of the package. Used almost exclusively in particulate or powdered form in gas permeable sachets.

3. Ascorbic acid (Vitamin C): Well known as an "oxygen interceptor." Ascorbic acid reacts rapidly with oxygen to form nutritionally inactive and innocuous compounds. Unlike iron, it does not respond to in-line metal detectors. Ascorbic acid requires moisture to function. It is a very expensive compound with relatively less capacity per unit mass than other scavengers.
4. Ligands or physical analogues of blood hemoglobin: These physically trap oxygen in "claw-like" chemical structures and are the basis for the Advanced Oxygen Technologies' technologies and patents. Limited capacities per unit mass in spite of their non-chemical method of oxygen removal. These ligands/ analogues are very expensive and so can add very significantly to the cost of the package material. Regulatory status is not clear.
5. Nylon MXD6: Together with cobalt catalysts, nylon MXD6 is the central oxygen reactant in Oxbar™ technology. Although the nylon itself is made in Japan or Europe, the total structure may be fabricated anywhere by blending with polyester package material. Oxbar™ is an extremely effective oxygen remover with high absorption capacity. It is capable of removing oxygen from a one liter bottle package headspace and then intercepting all oxygen entering by permeation for periods in excess of one year. The system is relatively easy to incorporate into thermoplastics. It is almost moisture insensitive. The cost can increase the price of package material structures by up to 20%. Regulatory status is not clear.
6. Light-sensitive anthoquinones: Developed by the Commonwealth Scientific Industrial Research Organization (CSIRO) in Australia. Not commercial but proposed for package wall structures. Regulatory status is not clear.
7. Enzymes: Although this category of oxygen absorbers received considerable publicity during the 1980s, technical and commercial development appear to be insufficient to warrant serious further investigation.

Very few of the commercial or proposed oxygen scavengers have actually been incorporated into the structure of a commercial package. Almost all oxygen scavenging has been by powdered chemical, e.g., reduced iron salt, ascorbic acid, glucose

oxidase/ catalase and gas/moisture permeable sachets placed within the package with moisture required for activation. The only exceptions have been ascorbic acid blended with plastic liner compounds in beverage bottle closures, and ligands blended with plastic liner compounds in beer bottle closures.

RECOMMENDATIONS

Several of the methods for incorporating oxygen scavenging materials into packaging materials appear to hold some promise for fabrication into flexible or semi-rigid package structures.

The key issue is whether enough oxygen scavenging capacity can be incorporated into a flexible or semi-rigid plastic package material structure, without significantly affecting the protective properties of the material and without potential toxic effects. Among the technologies are:

1. *Liquids trapped between two films:* Proposed and used in a number of test structures for other purposes. Suggested by both a W.R. Grace and a Scholle patent. Commercial in Japan for a non-scavenging application. The structure would contain a gas permeable membrane on the interior and a gas barrier on the exterior. With no headspace in the scavenging-containing compartment, this concept might possibly function, but the functioning would depend on the attitude or position of the package. The system is not believed to warrant further development.
2. *Powders trapped between two films, with the inner film being both gas and moisture permeable:* Depends on the orientation or physical position of the package; gravity causes the powder to move down when the package is vertical. Unless a method or proposal for immobilizing the powder is presented, this concept is not judged to warrant further development.
3. *Powders, such as reduced iron, enmeshed in a network trapped between two films, with the interior being gas and moisture permeable and the exterior a gas barrier:* The network may be a fibrous material such as a cellulose pulp or a plastic; or a microporous plastic material; or a spun-bonded microporous plastic such as DuPont's Tyvek® polyolefin. This type of structure has been proposed by numerous patents and researchers, and is the basis for Multiform Desiccant's FreshMax® flat label. The system appears to function well in the relatively limited confines of a finite label size; however, according to Multiform Desiccants, it is not yet adequate as a full package material, perhaps due to powder movement. This technology continues to be developed by Multiform Desiccants and warrants careful consideration as one means of creating oxygen scavenging package structures. In November 1994, Multiform Desiccants officially acknowledged that it had under development a plastic package material into which an oxygen scavenger had been incorporated. They predict a 1995 commercial introduction. It should also be noted that several Japanese companies including Mitsubishi Gas Chemical, Toyo Seikan

and Toray have patents, and undoubtedly patent applications and patents pending, on analogous-type package structures. Toyo Seikan has begun to commercialize their patent with Japanese food company Sato in a package for aseptically packaged rice. Their official position is that they are still in the development stage. Previously, wet rice had been packaged underreduced oxygen conditions in hermetically sealed trays with in-package oxygen scavenger sachets. Using the Toyo Seikan technology, the scavenger is between the polypropylene and the ethylene vinyl alcohol oxygen barrier of the base tray coextrusion. Perhaps the optimum strategy might be to take the best features of each of the Japanese technologies and marry them into a single structure. This concept appears to merit further investigation for commercial applicability.

4. *Powders, such as iron oxide, trapped in microvoids within cavitated core polyolefin films:* Materials such as polypropylene may be converted into opaque structures by nucleating and subsequently orienting to generate small voids. If the nucleating agent were partially substituted with an oxygen scavenger, the plastic could contain a uniform dispersion of oxygen scavenger. An external skin lamination of an oxygen barrier would be required if the material were a polyolefin. Alternatively, it may be possible to microvoid, i.e., foam, a fairly good gas barrier plastic such as polyester and thus incorporate the oxygen scavenger. This concept was proposed in a patent by Japan's Sumitomo Chemical for use with polyethylene. Although intriguing and with merit, our judgment ranks this concept as a possible complement to those in which the reduced iron powder or another oxygen scavenging counterpart is enmeshed in a plastic matrix (as in number 3 above).
5. *Microporous plastic beads blended physically into a continuous gas permeable plastic matrix:* According to Wm. Wrigley, the United States' chewing gum maker who suggested this concept, the plastic beads could be impregnated with an oxygen scavenger. This is an intriguing concept, but has little or no data to support the contention that the scavenger could be effectively incorporated into the microporous beads. Further, the advantage of the beads over direct incorporation of a scavenger into package material is not clear. No further study is warranted at this time.
6. *Blending of the compatible oxygen scavenger into a continuous plastic matrix:* These technologies may presuppose that the materials effectively blend and do not otherwise alter or diminish the desirable properties of the basic plastic materials. Several alternatives have been proposed including monolithic structures in which the oxygen scavenger is an integral component of the entire plastic structure, and multilayer structures in which the interior or contact surface is gas permeable and the exterior is a gas barrier. If the exterior is a

gas barrier, a relatively smaller quantity of oxygen from air will have to be reacted by the scavenger material. On the other hand, the monolithic material may be a gas barrier itself. A multilayer structure may be achieved by lamination, coextrusion or, for semi-rigid package structures, by coinjection followed by blowing. All of the blend proposals may be either monolithic or multilayer depending on the base material. In most instances, the proposals have focused on monolithic structures.

- a. Ligands are blended directly into the thermoplastic resins that may then be melted for extrusion and injection. These materials do not appear to be directly soluble in thermoplastics and are probably physically dispersed. The ligand technologies have generated so much publicity that they deserve a closer examination provided that the proprietary technology is available and the offering organization survives.
 - b. Unsaturated hydrocarbons should blend very effectively into polyolefin resins and not disrupt the physical chemical properties of the resins. This structure under development by W.R. Grace & Company in Lexington, Massachusetts, has optimistic long-term prospects by the developer. The company's spokesperson has indicated a desire to work with U.S. Army Natick R,D&E Center in the development, which they have projected to be several years away from commercialization. This development, which includes some elements of the developments of CSIRO in Australia, appears to be most interesting to pursue.
7. *Nylon MXD6/cobalt catalysts or Oxbar™*: This system is probably the most promising of all oxygen scavenger developments for packaging, regardless of type, due to data and demonstrations. The British origin will be overcome when an American partner officially discloses its active development program in the United States. The fact that the core reactant is either of Japanese or European origin should not be a deterrent since it constitutes less than 4% of the total package structure. Regulatory acceptance, which should be of some concern, can be obviated by multilayering until complete migration and toxicological data are generated. The compatibility of the oxygen scavenger with a fair gas barrier resin, such as polyester, permits the production of film, sheet and semi-rigid bottles and jars. The oxygen scavenger has the capacity to remove residual oxygen in the headspace and can intercept all oxygen permeating through the polyester base plastic for well in excess of one year. In our view, despite its current commercial shortcomings, this system warrants the major focus of U.S. Army Natick R,D&E Center's attention in the development of oxygen scavenging package structures.

APPENDICES

APPENDIX A

SURVEY FORM: END USERS OF OXYGEN AND MOISTURE SCAVENGERS

SURVEY FORM
END USERS OF
OXYGEN AND MOISTURE SCAVENGERS

	OXYGEN	WATER VAPOR
Do you use scavengers in the packaging for any of your products?		
Products/packages in which scavengers are used		
Timing--when introduced into the market		
Status		
Test marketing		
Commercial		
Regional		
National		
International		
Why is scavenger being used?		

	OXYGEN	WATER VAPOR
What is your source?		
Why did you choose this source?		
Have you changed sources or are you considering changing?		
If so, why?		
Are you considering use of scavenger in other products?		
Same end use or market		
Other end use or market		
Which of your competitors is using scavengers?		
For what products, to your knowledge, are any competitors considering scavengers?		
Shelf life required (at defined temperature/RH)		

	OXYGEN	WATER VAPOR
Is your package code dated?		
Is your package shipped overseas?		
Oxygen levels required inside of package		
Water vapor levels required on interior of package		
How is food treated after scavenger is added?		
Filling		
Distribution		
Reconstitution		
How much scavenger is used?		

	OXYGEN	WATER VAPOR
If a scavenger is used, how is your package material manufactured and by whom?		
Materials		
Process		
Flexible or rigid		
Package dimensions, volume, fill weight		
Driving forces for scavengers		
Price you pay for scavengers		
Problems experienced with scavengers scavengers?		
Other companies known that use in-package scavengers		
Name/Location		
Applications		

Your name_____ Title_____

Company Name _____

Address _____

Phone_____ Fax _____

Additional comments:

APPENDIX B

SURVEY FORM: SUPPLIERS OF OXYGEN AND MOISTURE SCAVENGERS

SURVEY FORM
SUPPLIERS OF
OXYGEN AND MOISTURE SCAVENGERS

Name_____ Title _____

Company _____

Address _____

Phone_____ Fax _____

Do you manufacture scavengers? _____

Oxygen _____

Moisture scavengers/absorbers _____

Other types _____

Trade name(s) _____

Location of manufacture _____

Since when have you
made scavengers? Oxygen:_____ Moisture: _____

Capacity and outputs Oxygen:_____ Moisture: _____

Chemistry of scavengers

Oxygen scavenger: _____

Moisture: _____

Other: _____

	OXYGEN	WATER VAPOR
Grades		
Advantages of your product		
Disadvantages of your product		
Prices and trends		
Regulatory status		
TECHNOLOGY In-house or Licensed		
Patent Nos., if any U.S. Foreign		
APPLICATIONS FOR YOUR PRODUCT		
End uses		
End users		

	OXYGEN	WATER VAPOR
APPLICATIONS (CONTINUED)		
When did they begin?		
Why is account using your product?		
Other accounts in same end use		
Do you market outside the U.S? If so, where?		
Do you manufacture outside the U.S? If so, where?		
Driving forces for scavengers		
OPPORTUNITIES AND GROWTH PROSPECTS FOR SCAVENGERS		
Overall		
Specific markets/ end uses		
Specific accounts		

	OXYGEN	WATER VAPOR
WHAT IS DELAYING GREATER GROWTH OF SCAVENGERS?		
Cost		
Performance		
Competitive technologies, if so which		
Other		
IMPORTS OF SCAVENGERS TO THE U.S.		
Application		
Who, to your knowledge, is importing?		
Technologies used		
End users, if known		

	OXYGEN	WATER VAPOR
HOW IS YOUR SYSTEM INCORPORATED IN A PACKAGE?		
Sachet		
Container walls		
Other		
Scavenging power of your system in terms of weight or volume of gas		
How is your scavenger activated?		
How is your scavenger prevented from prematurely activating?		
If in a sachet, what is the composition of the sachet?		
If a sachet, what insertion equipment source do you recommend?		

	OXYGEN	WATER VAPOR
PLASTIC PACKAGE FABRICATION How is scavenger incorporated?		
Extrusion		
Injection molding		
Blow molding Extrusion Injection		
Rotomolding		
Thermoforming		
If in container walls, how is it combined with plastic?		
Blending		
Compounding		
Other		

	OXYGEN	WATER VAPOR
Which technologies for plastic combination are used with your products?		
Food technologies usable with your scavengers Hot filling		
Retorting		
Aseptic filling		
Microwave heating		
Conventional oven heating		
Packaging systems usable with your scavenger technologies:		
Name		
Location		
Phone No. if known		
Contact person		
Applications		
Technology/chemistry		

Comments:

APPENDIX C
RELEVANT PATENTS

RELEVANT PATENTS

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